Synthesis of elevated temperature CO_2 adsorbents from aqueous miscible organic-layered double hydroxides

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Abstract

Layered double oxides (LDOs), which derives from the calcination of layered double hydroxides (LDHs), are a type of elevated temperature CO_2 adsorbents for pre-combustion carbon capture. Due to its highly aggregated stone-like structure, the CO_2 capture capacity of commercial MgAl-CO_3 LDO is relatively low. A novel method, the aqueous miscible organic solvent treatment (AMOST), was proposed to synthesize LDH precursors with increased surface area. In this work, three types of LDHs and LDOs with different Mg/Al ratios were synthesized using the conventional and AMOST methods. The aqueous miscible organic (AMO) solvent-treated Mg_2Al-CO_3 presented the highest CO_2 working capacity of 0.506 mmol/g at 400 °C of all the LDOs, which was 63.4% higher than that of commercial MG63. By removing the interlayered water using AMO solvent washing, the LDH was exfoliated into nanosheets and formed flower-like structures. The exposed internal surfaces increased the density of effective active sites after calcination. The AMO solvent-treated LDH also provided more alkali ion promoters for surface modification and led to better dispersion. After impregnation with 20 wt.% K_2CO_3, the CO_2 working capacity of the AMO solvent-treated K-Mg_3Al-CO_3 could reach a stable value of 1.069 mmol/g at 400 °C, which was 22.9% higher than that of commercial K-MG70.

Keywords

Layered double oxides; Elevated-temperature CO_2 adsorption; Aqueous miscible organic solvent treatment; Potassium impregnation; Pre-combustion carbon capture

1. Introduction

CO_2 emissions from the combustion of fossil fuels (coal, oil, and natural gas) have been widely recognized to aggravate environmental problems such as global warming and climate change in recent years, which led to an increased interests in developing new technologies for carbon capture, utilization, and storage (CCUS) [1,2]. The current carbon capture methods mainly include pre-combustion, post-combustion, and oxy-fuel combustion, where pre-combustion is related to gasification plants, post-combustion takes advantage of "end-of-pipe" characteristic in conventional coal-fired power plants, and oxy-fuel combustion is applied to new-built plants or retrofitted existing circulating fluidized bed plants [3,4]. The captured CO_2 can be stored via CO_2-enhanced oil recovery (EOR), enhanced gas recovery (EGR), depleted oil & gas fields, saline formations, ocean storage, and mineral storage, or alternatively, be utilized in food, beverage, and chemical industries, mineral carbonation, and cultivation of crops and algae [5].

Most of the commercial CCUS plants adopted post-combustion carbon capture methods that remove CO_2 from fuel gas using solvent absorption processes such as Selexol, NHD, Rectisol, MDEA, etc. [6]. However, the low CO_2 concentration in the fuel gas (less than 15%) leads to high capital costs and large equipment sizes. Owing to increased CO_2 concentration, the oxy-fuel combustion has a low carbon capture cost but the economic benefit is reduced by the costs of fuel gas recirculation and air separation [2]. Pre-combustion carbon capture using solid sorbents cuts down half of the operating costs that is required for post-combustion carbon capture due to higher capture pressure (2–7 MPa) and lower regeneration energy [7,8]. In addition, the solvent absorption processes usually work at normal or negative temperatures, and thus the syngas has to be pre-cooled before entering the separation unit and be re-heated after it. The concept of warm gas cleanup was proposed, which involves directly removing gas impurities, such as H_2S and CO_2, at elevated temperatures (200–400 °C) to avoid the sensible heat loss of syngas [9]. In the past decades, warm gas cleanup have attracted a great attention in pre-combustion CO_2 capture and high-purity H_2 production. Pilot-scale separation plants are being built worldwide, including the TDA's field demonstration unit (four-bed pressure swing adsorption) [10], the RTI's warm gas cleanup project [11], the ECN's technology (the latest project: STEPWISE) for sorption enhanced water gas shift [12], and the Shanxi Province Science and Technology Major Projects (MH2015-06) carried out by our research group [13].

The most common elevated temperature CO_2 adsorbents include layered double hydroxide (LDH) derived mixed oxides and MgO-based sorbents [14,15]. LDHs belong to brucite-like 2D anionic materials with a general formula of $[\mathrm{M}_x^{2+}\mathrm{M}^{3+}(\mathrm{OH})_{2x+2}]^{+}(\mathrm{A}^{n-})_{1/n}\cdot m\mathrm{H_2O}$, where M^{2+} and M^{3+} represent divalent and trivalent cations, respectively, and A represents the interlayered anion. LDHs are widely used as precursors for CO_2 adsorption , catalysts, as well as in biomedicine, electrochemistry, and for water treatment [16]. Upon thermal treatment, such as dehydration (70–190 °C), dehydroxylation (190–405 °C), and decarbonation (405–580 °C) [17], LDHs transform into layered double oxides (LDOs) which exhibit numerous active sites including low-, medium-, and high-basicity sites [18]. The unsaturated Mg-O sites generated by the substitution of divalent cations with trivalent cations and the diffusion of divalent cations out of the octahedral lattice during calcination were reported to be the main elevated temperature CO_2 active sites [19]. The CO_2 adsorption capacity of LDOs could be further enhanced after surface modification using alkali (K and Cs) doping [20].

Since the 2000s, there has been an increasing interest in synthesizing and characterizing LDHs-derived mixed oxides as elevated temperature CO_2 adsorbents. Studies have included replacing cations or anions [21], changing the x ratio [22], as well as different preparation methods [23], calcination temperatures [19], working temperatures and pressures [24], the effect of SO_x/H_2S and H_2O [25], alkali (K and Cs) doping [20], particle size [26], and supports effect [27]. In general, however, the CO_2 adsorption capacities of MgAl-CO_3 LDOs and K_2CO_3 doped LDOs at 200–400 °C have only been 0.5 and 0.8 mmol/g, respectively [21], which are insufficient for commercial utilization. One reason for the low CO_2 adsorption capacities is the LDH precursors being highly aggregated and presenting a stone-like morphology, which leads to relatively low surface areas. To expose more surface sites, Qiang et al. [28] intercalated organic anions with long carbon chains and low decomposition temperatures into the Mg_3Al-CO_3 LDH and expanded its interlayer distance from 0.78 to 3.54 nm. After thermal treatment, the decomposition of organic anions caused the collapse of the layered structure into a disordered microstructure and generated a plate-like morphology with lower crystallinity and smaller particle size. The CO_2 adsorption capacity of the Mg_3Al-stearate LDO reached 1.15–1.25 mmol/g at 200–400 °C, which was twice as large as that of the Mg_3Al-CO_3 LDO. Later, they investigated the effect of the length of the carbon chain of the organic anions and demonstrated that the CO_2 adsorption capacity increased as the number of carbon atoms increased from 8 to 16 [29]. The expanded gallery height also increased the chance of the alkali ions diffused into the interlayers to interact with the hidden basic sites. For instance, Li et al. [30] introduced 12.5 wt.% K_2CO_3 into the Mg_3Al-stearate LDH precursor and determined that the CO_2 adsorption capacity of the K-Mg_3AlCO_3-stearate LDO increased to 1.93 mmol/g at 300 °C, which was 1.7 times the capacity of the K-Mg_3Al-CO_3 LDO.

Other possible methods to increase the surface area would be to directly exfoliate the LDH into layers or thin nanosheets using “bottom-up” or “top-down” methods [31]. However, due to their high surface charge and hydrophilicity, the exfoliated LDH layers in the solvent would be able to easily re-stack after drying [32]. To stabilize the exfoliated LDH layers, Garcia-Gallastegui et al. [33] adopted graphene oxide (GO) as support. The positively charged LDH layers were found to disperse well onto the negatively charged GO flakes, forming “layer-by-layer” structures with either double-sided or single-sided coatings. The CO_2 adsorption capacity of the LDO/GO hybrid materials increased to 62% by adding only 7 wt.% GO. Recently, O’Hare’s group reported another feasible method that could simply exfoliate LDH into small plates without supports, which was called the aqueous miscible organic solvent treatment (AMOST) [32,34]. The idea was that during a co-precipitation synthesis procedure, AMO solvents such as acetone and methanol were adopted to wash the wet LDH slurry and to remove the interlayer water. The induced solvents evaporated during the subsequent vacuum drying, allowing the LDH plates to slide easily. The AMOST method could lead to the exfoliation of LDH into nanosheets or even single layers. For instance, after AMOST (washing with acetone), the Zn_2Al-borate LDH exhibited an extremely high surface area of 458.6 m^2/g and large pore volumes of 2.15 cm^3/g [32]. The effects of the composition, synthesized pH, and AMO solvent on the physical properties of AMO treated LDHs (AMO-LDHs) have been investigated [34]. The AMOST method was also used to synthesize core–shell materials with silica and zeolite as core materials and LDHs as shell materials, which might present superior catalytic performances [35].

To date, the applications of AMO-LDHs-derived mixed oxides for CO_2 capture have not been reported yet. In this work, three types of MgAl-CO_3 LDHs and LDOs with different Mg/Al ratios were synthesized using both the conventional and AMOST methods. The structure of the material, surface properties, morphology, as well as the CO_2 capture capacities were systematically investigated to understand the improvement of the CO_2 working capacity and kinetics of LDOs after AMOST. The effect of K_2CO_3 impregnation and the distribution of K_2CO_3 on the surface of AMO-LDOs were also studied and discussed.

2. Experimental section

2.1. Preparation of LDHs and LDOs

The co-precipitation method was adopted to synthesize all the LDHs in this work. All the chemicals, including $Mg(NO_3)_2 \cdot 6H_2O$ (AR), $Al(NO_3)_3 \cdot 9H_2O$ (AR), Na_2CO_3(AR), NaOH (AR), acetone (99.8%), K_2CO_3(AR), were purchased from Sigma-Aldrich Co.

LLC., and were used without further purification. For the synthesis of conventional LDH (C-LDH), the metal source (100 mL) containing 1 M total metal ions of $Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ was added to 100 mL of 0.5 M Na_2CO_3 aqueous solution at a constant dropping rate of 100 mL/h and under vigorous stirring. The Mg/Al molar ratios of the LDHs were maintained the same as those of the commercial MG30 (Mg/Al ratio of 0.55), MG63 (Mg/Al ratio of 2), and MG70 (Mg/Al ratio of 3), which were obtained from Sasol, Germany. The pH was controlled to 10.0 ± 0.1 by adding 4 M NaOH aqueous solution. The suspension was then aged at room temperature for 16 h under a stirring rate of 500 rpm. Afterward, the mixture was filtrated and washed with deionized (DI) water until pH 7. For synthesizing AMO-LDH, the wet LDH cake was rinsed with 1000 mL acetone before it became dry. The rinsed LDH solid was re-dispersed into 600 mL acetone, stirred at 800 rpm for 4 h, and filtrated after washing with another 400 mL of acetone. Both LDHs were finally dried in a vacuum oven overnight.

The K_2CO_3 doped LDHs (K-LDHs) were synthesized using the impregnation method. First, 0.8 g K_2CO_3 was dissolved into 15 mL DI water, and then the solution was added to 4 g of LDH. The suspension was stirred for 3 h followed by drying in air at 105 °C overnight. The LDOs/K-LDOs were synthesized by *ex situ* calcining the LDHs/K-LDHs precursors in a muffle furnace at 450 °C for 3 h. Fig. 1 illustrates the diagram of the synthetic process used in this work.

Fig. 1. Diagram of synthetic process of AMO-LDO and K-AMO-LDO.

For convenience, the synthesized sample was named K-Mg_xAl-CO_3-S(c), where x is the Mg/Al ratio, S is the treating method (“w” for water washing, “a” for acetone washing, and “S” for Sasol, for commercial LDH obtained using the sol-gel method), the optional K represents the K_2CO_3 impregnation treatment, and the optional (c) represents the calcination treatment.

2.2. Material characterization

Powder X-ray diffraction (XRD) analyses were conducted on a PANalytical XPert Pro diffractometer in reflection mode using Cu Kα radiation and a power of 40 kV × 40 mA. Scans were recorded from 3 to 70° with a step size of 0.02°. N_2 adsorption and desorption isotherms at 77 K were obtained using a Micromeritics TriStar II plus instrument. The specific surfaces and pore volumes were analyzed using the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) desorption methods, respectively. Before each measurement, the samples were degassed overnight at 110 °C. Scanning electron microscopy (SEM) was performed at 20 kV on a JEOL JSM-6610LV instrument with energy dispersive spectroscopy (EDS). Transmission electron microscopy (TEM) was conducted on a JEOL 2100 device at 200 kV. Samples synthesized using the conventional and AMOST methods were dispersed in DI water and acetone, respectively, while sonicating them for 15 min, and then casted onto copper grids. The thermal decomposition behaviors of the samples were measured by thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTG) using a TGA/DSC 1 instrument (Mettler Toledo). Approximately 20 mg of each sample was heated in a corundum crucible from room temperature to 450 °C at a heating rate of 10 °C/min under 100 mL/min of N_2 flow.

2.3. CO_2 capture capacity evaluation

The CO_2 adsorption/desorption performance was evaluated on a Q600 TGA (TA Instruments). Approximately 10 mg of each sample was placed in a corundum crucible and was *in situ* calcined under 100 mL/min N_2 flow at 450 °C for 1 h to avoid the recovery of LDH structures when exposing to ambient atmosphere (memory effect) [36]. Higher calcination temperatures are not suitable to synthesize LDOs because of the formation of spinel phase with decreased surface areas [19]. Afterward, the temperature was decreased to the working temperature and the feed gas was alternately switched between 300 mL/min CO_2 for adsorption and 300 mL/min N_2 for desorption. Both the adsorption and desorption times were set at 1 h. The performance of the CO_2 adsorbents was evaluated using the CO_2 working capacity in Eq. (1). As proposed by Coenen et al. [25,37–39], the CO_2 working capacity took into consideration both the adsorption and desorption capacities, and was more accurate for evaluating the cyclic capacities in pressure swing adsorption (PSA) processes compared to using the CO_2 adsorption capacity alone.

$$q_{\mathrm{CO_2}} = \frac{\mathrm{abs}(\Delta m_{\mathrm{ads}})+\mathrm{abs}(\Delta m_{\mathrm{des}})}{2M_{\mathrm{CO_2}}m_{\mathrm{sample}}} \quad (1)$$

In the above equation, $q_{\mathrm{CO_2}}$ represents the CO_2 working capacity (mmol/g); Δm_{ads} and Δm_{des} represent the weight changes of sample during CO_2 adsorption and desorption, respectively (g); $M_{\mathrm{CO_2}}$ represents the molar mass of CO_2 (mmol/g); and m_{sample} represents the initial sample weight (g).

3. Results and discussion

3.1. Physical properties

The XRD results in Fig. 2(a) demonstrated that the C-LDHs and AMO-LDHs were successfully synthesized. All the samples exhibited typical LDH patterns, and all the calcined samples exhibited LDO patterns including only weak MgO peaks (Fig. 2(b)). The peak positions of LDHs did not change after AMOST. When decreasing the Mg/Al ratio from 3 to 2, the 003 peaks of both C-LDH and AMO-LDH shifted from 11.43 to 11.63° and the 006 peaks shifted from 22.86 to 23.28°. This was due to the higher layer charge density shortening the interlayer distance. When further decreasing the Mg/Al ratio to 0.55, no obvious peak shift was observed, but small peaks at approximately 20° appeared. Therefore, it was assumed that $Mg_{0.55}Al-CO_3$ was a combination of LDH with a Mg/Al ratio close to 2 and Al-containing impurities. After calcination, the impurities decomposed to Al_2O_3, which distributed uniformly throughout the LDOs.

Fig. 2. (a) XRD patterns of LDHs (Mg/Al ratios of 0.55, 2, and 3; * are reflections of the sample holder); (b) XRD patterns of LDOs (Mg/Al ratios of 0.55, 2, and 3); (c) N_2 isotherms and pore distributions of LDHs and LDOs (Mg/Al ratio of 3); and (d) thermal decomposition curves of LDHs (Mg/Al ratio of 3).

Fig. 2 includes several pieces of evidence on the differences between C-LDHs and AMO-LDHs [34]. First, the 003 and 006 peaks of the AMO-LDHs were lower than those of the C-LDHs, indicating that the AMOST decreased the crystallinity of LDH and allowed it to easier form a disordered structure. The peaks did not disappear completely like those of acetone washed Mg_3Al-borate LDH did [32], probably due to CO_3^{2-} presenting a stronger interaction with the LDH layers. Second, the N_2 isotherms and pore distributions for LDHs and LDOs are illustrated in Fig. S1 (Mg/Al ratio of

0.55 and 2, Supporting Information) and Fig. 2(c) (Mg/Al ratio of 3). All samples exhibited typical type IV isotherms with H3 hysteresis loops, which are associated with slit-shaped mesopores on plate-like particles [40]. However, the average mesopore volume of AMO-LDH of approximately 10 nm was much higher than that of C-LDH, and was further expanded after calcination. Third, the thermal decomposition curves of LDHs between room temperature and 450 °C are shown in Fig. S2 (Mg/Al ratio of 0.55 and 2) and Fig. 2(d) (Mg/Al ratio of 3). The LDHs exhibited two weight loss stages: the first stage at approximately 200 °C (T_1) corresponding to the desorption of intercalated solvents and the second stage at approximately 400 °C (T_2) for the decomposition of hydroxyl and carbonate [34]. Both T_1 and T_2 were decreased after AMOST due to a better dispersion of the LDH layers.

The morphologies of LDHs were studied using TEM with an amplification factor of 20 000 (Fig. 3). Due to their high surface charges and hydrophilicity, all C-LDHs exhibited highly aggregated, stone-like structures. After AMOST, the removal of the interlayered water weakened the interaction between the LDH plates, and flower-like structures consisting of much thinner layers were formed. When the Mg/Al ratios were reduced from 3 to 0.55, the increasing Al content broke the perfect brucite-like structure of the LDH layers, thus decreasing the diameter of the AMO-LDH plates. After calcination, the morphologies of the AMO-LDOs did not change, but the release of CO_2, H_2O, and solvents generated porous layers. The surface area and pore volume of LDHs and LDOs with Mg/Al ratio of 0.55, 2, and 3 were listed in Table 1, and the average pore size was listed in Table S1. The exfoliation of the AMO-LDHs resulted in high surface areas and large pore volumes [41]. For instance, the surface area of Mg_3Al-CO_3-a tripled (158 m^2/g) and its pore volume doubled (0.83 cm^3/g) compared to Mg_3Al-CO_3-w. After optimization of AMOST and drying methods, Mg_3Al-CO_3-a could even achieve a surface area of 365 m^2/g [41]. The surface area of AMO-LDH increased as the Mg/Al ratio decreased because of the reduced LDH particle size. After calcination, all AMO-LDOs reached surface areas of approximately 300 m^2/g and pore volumes larger than 1 cm^3/g. It should be noted that the crystallinity of LDHs decreased with the decrease of the aging temperature [26]. Therefore, the platelet sizes and surface areas of the synthesized LDHs using room temperature as the aging temperature were much lower than that of the Sasol-LDHs synthesized using sol-gel methods. On this basis, the AMOST further exfoliated the interlayered surface area to expose more active sites.

Fig. 3. TEM of LDHs (Mg/Al ratios of 0.55, 2, and 3) and LDO (Mg/Al ratio of 3).

Table 1. Surface area of LDHs and LDOs (Mg/Al ratios of 0.55, 2, and 3).

Fig. 4 illustrates that after impregnating 20 wt.% K_2CO_3, the typical peaks for LDHs and LDOs still existed, but additional peaks for K_2CO_3 at approximately 30–35° were observed for all the samples. The morphologies of K-LDHs and K-LDOs are presented in Fig. S3 (Mg/Al ratios of 0.55 and 2) and Fig. 5 (Mg/Al ratio of 3). Although partial reconstructions occurred during the impregnation procedure due to the samples coming into contact with water, the K-AMO-LDHs and K-AMO-LDOs still exhibited exfoliated flower-like structures. The elemental analysis of K-Mg_3Al-CO_3-a demonstrated the presence of two morphologies of impregnated K_2CO_3: the bulk phase K_2CO_3 that was located in the cubic area, and the scattered K_2CO_3 that was uniformly distributed on the surface of K-LDH and possibly modified the active sites.

Fig. 4. (a) XRD patterns of K-LDHs (Mg/Al ratios of 0.55, 2, and 3; * are reflections of the sample holder); (b) XRD patterns of K-LDOs (Mg/Al ratios of 0.55, 2, and 3).

Fig. 5. TEM of K-LDHs and K-LDOs (Mg/Al ratio: 3).

Previous studies mentioned that the gallery height of C-LDH (0.28 nm) was similar to the size of K^+ (0.276 nm) [30], and thus surface modification was mainly limited to the external surface of the LDH particles. However, after AMOST, the internal surface of LDH was exposed, and presented an increased amount of possible K^+ promoters. Therefore, K_2CO_3 was supposed to modify more active sites on the surface of K-AMO-LDH [30]. To further investigate the effect of surface modification on K-AMO-LDH, the SEM micrographs of K-Mg_3Al-CO_3-Sasol, K-Mg_3Al-CO_3-w, and K-Mg_3Al-CO_3-a before and after calcination illustrated in Fig. 6 were analyzed. The red spots represent the elemental K detected by EDX scans. The K-AMO-LDH presented the least amount of areas with concentrated red spots of the three types of K-LDHs, which indicated that K_2CO_3 had the tendency to modify the surface sites of K-AMO-LDH rather than to remain a bulk phase.

Fig. 6. SEM of K-LDHs and K-LDOs (Mg/Al ratio of 3).

3.2. CO_2 capture properties

3.2.1. Effects of AMOST

Fig. 7 exhibits the CO_2 working capacity of Sasol-LDOs, C-LDOs and AMO-LDOs tested at 400 °C. The results indicated that when using the same synthesis method, LDOs with a Mg/Al ratio of 2 presented the highest CO_2 working capacity, which was consistent with the results reported in the literature [42]. The unsaturated Mg-O sites were believed to be the CO_2 adsorption sites for LDOs [19]. When the Mg/Al ratio decreased, the total number of Mg-O sites decreased. On the other hand, the increased amount of Al^{3+} created more defects in the LDH layers, causing the Mg-O sites to become more active to react with CO_2. For the same Mg/Al ratio, the CO_2 working capacity of LDOs was positively related to the surface area. The Mg_2Al-CO_3-a(c) exhibited the highest CO_2 working capacity of 0.506 mmol/g of all the LDOs, which was 63.4 and 14.0% higher than those of Mg_2Al-CO_3-Sasol(c) (0.309 mmol/g) and Mg_2Al-CO_3-w(c) (0.444 mmol/g), respectively.

Fig. 7. CO_2 working capacity of LDOs at 400 °C (Mg/Al ratios of 0.55, 2, and 3).

The temperature effect on the CO_2 adsorption/desorption performance of C-LDOs and AMO-LDOs is illustrated in Fig. 8. When the working temperature was decreased from 400 to 200 °C, the CO_2 adsorption capacity of the LDOs increased as reported by other studies [43,44]. In all the samples there was a fast CO_2 uptake followed by a slower adsorption, which fitted well with the Elovich-type kinetic model [45]. On the other hand, decreasing the temperature presented unfavorable effects on the kinetics of the desorption process. To guarantee the cyclic operation in a PSA system, the CO_2 desorption to adsorption ratio should be as high as possible. There was no obvious improvement on the CO_2 adsorption kinetics after AMOST. However, the AMO-LDOs presented superior desorption kinetics (Table 2), probably due to better mass transfer performances of CO_2 from the surface of exfoliated layers to the gas phase. The larger

CO_2 desorption to adsorption ratio of the AMO-LDOs extended their working temperature range. The results in Fig. 8(d) demonstrated the AMO-LDOs achieved higher CO_2 working capacities than C-LDOs for all working temperatures.

Fig. 8. Temperature effects on CO_2 adsorption/desorption performance of LDOs (Mg/Al ratios of 0.55, 2, and 3).

Table. 2. CO_2 desorption to adsorption ratios of LDOs with different working temperatures (Mg/Al ratios of 0.55, 2, and 3).

3.2.2. Effects of K_2CO_3 impregnation

Surface modification using alkali metals compounds such as X_2CO_3 (X = K and Cs) and YNO_3 (Y = Li, Na, and K) was commonly adopted to enhance the CO_2 capture ability of LDOs. In this section, the effects of 20 wt.% K_2CO_3 impregnation on AMO-LDOs were investigated. Fig. 9 depicts the CO_2 working capacities of K-Sasol-LDOs, K-C-LDOs, and K-AMO-LDOs at 400 °C. Unlike the results obtained for LDOs, the CO_2 working capacities of the K-LDOs increased as the Mg/Al ratio increased. This positive correlation indicated that after the surface modification of the K_2CO_3 impregnation, the total amount of exposed Mg-O active sites became the critical factor for the CO_2 capture ability of K-LDOs. For a set Mg/Al ratio, the K-AMO-LDO and K-Sasol-LDO exhibited the highest and lowest CO_2 working capacities, respectively, which was consistent with the results obtained for LDOs. It can be concluded that the formation of dense and well-dispersed surface sites modified by K_2CO_3 after calcination increased the chance of K-AMO-LDO to react with CO_2.

Fig. 9. CO_2 working capacities of K-LDOs at 400 °C (Mg/Al ratios of 0.55, 2, and

3).

The long-term stability of K-LDOs with a Mg/Al ratio of 3 is displayed in Fig. 10. All the samples presented an area of irreversible capacities during the first cycle, which caused a lower CO_2 working capacity compared to the adsorption capacity. Afterward, however, both the adsorption and desorption capacities reached stable values. The K-Mg_3Al-CO_3-a(c) sample presented the highest CO_2 working capacity of 1.069 mmol/g after ten adsorption/desorption cycles which was 22.9 and 26.4% higher than those of K-Mg_3Al-CO_3-Sasol(c) (0.870 mmol/g) and K-Mg_3Al-CO_3-w(c) (0.846 mmol/g), respectively. In previous work we proved that a 20% increase of CO_2 adsorption capacity increased 5% CO_2 capture ratio in a four-column pressure swing adsorption [46]. Therefore, we believe that improving the CO_2 working capacity of LDOs/K-LDOs using the AMOST method is meaningful in industrial applications for CCUS.

Fig. 10. (a) CO_2 uptake and (b) CO_2 working capacity of K-LDO at 400 °C as a function of the number of cycles (Mg/Al ratio of 3).

4. Conclusions

AMO-LDHs with different Mg/Al ratios were successfully synthesized in this work. By washing the LDHs with acetone during the co-precipitation process, the LDH layers were exfoliated and formed flower-like structures with increased surface areas. The exposed internal surfaces provided denser active sites after calcination. The novel method of AMOST was quite simple since the only difference between it and the conventional co-precipitation method was the introduction of AMO solvent-washing step. The increased costs of AMOST mainly came from the consumption of AMO solvents. However, in the large-scale industrial synthesis, the solvents could be recycled after purification. The CO_2 working capacities of AMO-LDOs at 400 °C were higher than those of both Sasol-LDOs and C-LDOs, and Mg_2Al-CO_3-a(c) reached the highest value of 0.506 mmol/g (400 °C) among all the investigated LDOs. AMO-LDOs also exhibited better desorption kinetics compared to C-LDOs at 200–400 °C. Another benefit of AMO-LDH was that it provided more promoters for surface modification. After 20 wt.% K_2CO_3 impregnation, the K^+ preferred to well disperse on the surface of the AMO-LDH rather than to form bulk phase K_2CO_3. The CO_2 working capacities of K-LDOs were positively related to the total amount of exposed Mg-O sites. After a ten-cycle adsorption/desorption test, the CO_2 working capacity of K-Mg_3Al-CO_3-a(c) reached a stable value of 1.069 mmol/g (400 °C), which was 22.9 and 26.4% higher than those of K-Mg_3Al-CO_3-Sasol(c) and K-Mg_3Al-CO_3-w(c), respectively. This improvement was believed to largely improve the separation efficiency of pressure swing adsorption units. In the following work, the AMOST method should be optimized by changing the process parameters and AMO solvents to achieve better CO_2 adsorption/desorption performance.

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