High-Temperature Adsorption of Carbon Dioxide on Mixed Oxides Derived from Hydrotalcite-Like Compounds

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Various X_nY_{3-n} Al-hydrotalcite-like compounds (HTlcs) were synthesized by the constant pH coprecipitation method with the $(X^{2+} + Y^{2+})/Al^{3+}$ molar ratio fixed at 3.0. Well-mixed oxides $X_nY_{3-n}AlO$ were derived from corresponding HTlcs precursors upon calcination. Physicochemical characterization with X-ray diffraction analysis, Fourier transform infrared spectroscopy, thermogravimetric analysis (TGA), and the Brunauer–Emmett–Teller equation indicates that the derived oxides are of either periclase or spinel phase, with an interparticle pore diameter of 9.6–15.4 nm. These oxides generally show a high CO_2 adsorption capability at 350 °C. For example, $CaCoAlO$ captures 1.39 mmol/g of CO_2 (i.e., 6.12 wt %) from a gas mixture (8% CO_2 in N_2) at 350 °C and 1 atm in a fixed-bed reactor within 20 min. All other mixed oxides adsorb 0.87–1.28 mmol/g (3.83–5.63 wt %) of CO_2 . Therefore, these mixed oxides are potential cost-effective CO_2 sorbents for environmental remediation. In addition, the CO_2 adsorption behavior is well-described with the deactivation model. The species of CO_2 formed on the sorbents are various carbonates, as revealed by *in situ* IR spectra as well as TGA.

Introduction

Fossil fuels are the major source of energy we use everyday. The combustion of fossil fuels releases CO_2 to the environment, which has caused some severe global problems, such as global warming and weather fluctuation (1). A feasible way to mitigate the impact is to capture CO_2 from industrial flue gases with an inexpensive adsorbent and then bury it underground (2). Since the flue gas from a coal burner is very hot (around 400–600 °C), it is highly desirable to adsorb CO_2 at high temperatures without cooling to room temperature, which makes the overall processes more feasible and more economic. However, most commonly used inorganic materials, such as zeolites and activated carbons, show a

dramatic decrease in CO_2 sorption capacity with an increase in the adsorption temperature due to their physical adsorption features (3, 4). A promising candidate is activated hydrotalcite-like compounds (HTlcs) that efficiently take up CO_2 at higher temperatures (5–8) and dramatically improve the sorption capacity of CO_2 when coated on zeolite (9).

HTlcs, known as anionic clays or layered double hydroxides, are multifunctional materials that are widely used as adsorbents, ion exchangers, base catalysts, and precursors of well-mixed oxides for various catalytic applications (10). HTlcs can be chemically expressed by a general formula $M_{(1-x)}^{2+}M_x^{3+}(OH)_2A_x \cdot nH_2O$ ($x = 0.2–0.4$), where M^{2+} and M^{3+} represent most divalent and trivalent metal ions or their combination, and A^- any hydrated anion (10). Therefore, HTlcs and derived oxides are almost unlimited in composition, so that one can select a set of cations to make HTlcs and finely manipulate their properties for a particular purpose. For example, the derived well-mixed oxides (namely, activated HTlcs) were designed as particular catalysts for the synthesis of many organic molecules (10). As sorption materials, activated $MgAl$ –HTlcs have recently been found to have a high sorption capacity for CO_2 (5, 7, 8). However, many other HTlcs-derived oxides, such as those containing Ca and transition metal ions, have not been investigated for this purpose thus far.

In our previous studies (11, 12), we prepared a number of well-mixed oxides as cost-effective NO_x storage/reduction catalysts. We noted that over these particular Ca-containing oxides NO adsorption was severely prohibited by competitive CO_2 adsorption; that is, these oxides favorably take up CO_2 . This observation motivated us to investigate the CO_2 sorption properties of these Ca- and Co-containing oxides at a high temperature (350 °C) in this research. This temperature was selected because we considered that (1) the flue gas is very hot (400–600 °C), (2) the CO_2 capture by HTlcs-derived oxides is chemical, reaching a maximum amount at 300–450 °C (5, 7, 8), and (3) our preliminary experiments show that there is a maximum CO_2 sorption of Ca-containing mixed oxides at around 350–400 °C. In the tests, a fixed-bed reactor was used to investigate CO_2 adsorption, which reveals that $CaCoAl$ -oxide takes up 1.39 mmol of CO_2 per gram of the oxide, that is, 6.12 wt % at 350 °C in a N_2 stream containing 8% CO_2 at ambient pressure.

Experimental Section

Materials Preparation. Various $Mg_xCo_yCa_zAl$ ($x + y + z = 3$) HTlcs were synthesized using the coprecipitation method (denoted as $Mg_xCo_yCa_zAl$ -HTlc). First of all, a mixed salt solution (150 mL) containing a stoichiometric atomic ratio (Table 1) of $Ca(NO_3)_2 \cdot 4H_2O$ (>99%, Yili company), $Co(NO_3)_2 \cdot 6H_2O$ (>99%, Jinke company), $Mg(NO_3)_2 \cdot 6H_2O$ (>99%, Yili company), and $Al(NO_3)_3 \cdot 9H_2O$ (>99%, Yili company), and a solution (150 mL) of $NaOH$ (>96%, Beihua company) and Na_2CO_3 (>99.8%, Beihua company) with $[OH^-]/[CO_3^{2-}] = 16$ and $[OH^-]/[Al^{3+}] = 8$, were separately prepared with doubly distilled water. These two solutions were then simultaneously added dropwise into 100 mL of doubly distilled water within 1 h at constant pH (10 ± 0.5) under vigorous mechanical stirring. The precipitate was aged in suspension at 60 °C for 4 h under stirring in static air and filtered and thoroughly washed with doubly distilled water. The cake was dried at 70 °C for 12 h and again at 120 °C overnight. As-prepared HTlcs were calcined at 550 °C for 4 h to derive the corresponding mixed oxides, as denoted in Table 1. The oxides were then crushed and sized in 20–40 mesh for CO_2 adsorption

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TABLE 1. Composition, Textural Property, CO₂ Capture Amount, and Simulated Parameters of Oxide Sorbents

sample	atomic ratio of cation	SSA (m ² /g)	pore size (nm)	pore volume (cm ³ /g)	capture amount (mmol/g)	κ_0 (cm ³ /min g)	κ_d (min ⁻¹)
MgAlO	3:1	161	9.8	0.40	1.13	148.7	0.51
CoAlO	3:1	96	9.6	0.23	1.03	162.6	0.68
CaAlO	3:1	26	14.0	0.09	0.87	163.2	0.59
CoMgAlO	1.5:1.5:1	127	14.1	0.45	1.05	170.3	0.63
MgCaAlO	2:1:1	253	15.4	0.98	1.28	180.6	0.54
CaCoAlO	1.5:1.5:1	91	10.6	0.24	1.39	212.5	0.55

experiments and kept in a desiccator in order to avoid any contamination from the air.

Materials Characterization. The X-ray diffraction (XRD) patterns of precursors and the derived mixed oxides were recorded on a Rigaku powder diffractometer (D/MAX-RB) by using Cu K α radiation ($\lambda = 0.15418$ nm) in a 2θ range of 10–70° at a scanning rate of 4°/min. The tube voltage and current were set at 40 kV and 30 mA, respectively. Thermal decomposition behaviors of as-prepared HTlcs were investigated with thermogravimetric analysis (TGA; Seteram, Labsys). In a typical measurement, 20–30 mg of HTlc sample was heated in an Al₂O₃ crucible at a heating rate of 10 °C/min from 25 to 1000 °C, with air purging at a flow rate of 30 mL/min. The textural properties of derived mixed oxides were analyzed by N₂ adsorption/desorption at liquid-nitrogen temperature (77 K), using a gas adsorption analyzer, Quantachrome NOVA-1200. The specific surface area (SSA) was calculated with the Brunauer–Emmett–Teller (BET) equation, while the pore volume and pore size distribution were obtained with the Bopp–Jancso–Heinzinger method from the adsorption isotherm.

CO₂ Adsorption Activity. Thermal CO₂ adsorption experiments were carried out in a quartz fixed-bed flow-reactor (i.d. = 8 mm and $L = 600$ mm) using 1.0 g oxide sorbent (20–40 mesh powder) at atmospheric pressure. The oxide sorbent was pretreated at 500 °C for 1 h with N₂ flowing at 50 mL/min. After cooling down to 350 °C, a stream mixture of CO₂ and N₂ with 8% CO₂ at a total flow rate of 50 mL/min was passed through the fixed bed. The space velocity was kept at approximately 3000 h⁻¹. The adsorbent bed was heated on a tubular furnace, and the temperature was monitored with a thermocouple inserted into the bed. CO₂ in the outlet was monitored online by a gas chromatograph (GC) equipped with a 60/80 Carboxen 1000 column (15 ft $\times$ 1.25 in. s.s.) through catalytically converting CO₂ to CH₄ with a Ni catalyst mounted in a catalytic furnace prior to the flame ionization detection measurements. The CO₂ concentration in the outlet was thus calculated by integrating the GC peak area. The CO₂ sorption amount was further calculated from the CO₂ sorption profile by considering the CO₂ flowing profile without any oxide sorbent mounted in the reactor (used as a blank).

To test the accuracy of the CO₂ sorption amount calculated with the above method, we used TGA to determine the direct CO₂ sorption amount, as usual (7). In this TGA test, about 40 mg of an oxide sorbent was placed in the sample pan. Similarly, the sample was first pretreated by passing pure N₂ at 30 mL/min for 30 min at 500 °C, then cooled down to 350 °C. CO₂ sorption was carried out by switching the purge gas from N₂ to a CO₂/N₂ gas mixture at 350 °C, and this was continued for 18 h until the sorption equilibrium was reached.

In Situ Infrared Monitoring. The *in situ* Fourier transform infrared spectroscopy (FTIR) spectra were recorded on a Bruker Tensor 27 spectrometer in the range of 600–4000 cm⁻¹ after 128 scans at a resolution of 4 cm⁻¹. Self-supporting pellets (~50 mg, 20–40 mesh) were prepared

from the oxide sorbents and used directly in the IR flow cell. The IR cell made of stainless steel contains a KBr window and is connected to a vacuum apparatus with a residual pressure below 10⁻⁴ Pa. A K-type thermocouple was set in direct contact with the IR flow cell to monitor the temperature. A Harric series 999 temperature controller was used to control the experimental temperature. Prior to the IR spectrum recording, the oxide sample was flushed with pure N₂ for 10 min and then pumped off for 1 h at 400 °C (the maximum temperature that the setup can tolerate). After the temperature was cooled down to 350 °C, the spectrum of the treated sample was taken as the background. Then, a mixture gas stream containing 8% CO₂ in N₂ was introduced at 25 mL/min for CO₂ adsorption at 350 °C, and the IR spectra were sequentially recorded at time points of 1, 2, 5, 10, 20, 25, and 30 min.

Results and Discussion

Structural Effects of Cations on HTlcs and Derived Oxides.

The X-ray diffraction patterns of as-prepared HTlcs (dried at 120 °C) are shown in Figure 1A. The precursors MgAl- and CoAl-HTlc exhibit the typical X-ray diffractogram of hydroxalcalite. The peaks at $2\theta = \sim 11^\circ$, 23° , and 34° corresponding to the (003), (006), and (009) crystal planes indicate the well-formed crystalline layered structure with a rhombohedral symmetry (3R) (9), and the broad diffraction peaks at $\sim 35^\circ$, 38° , and 46° attributed to (012), (015), and (018) crystal planes are characteristic of polytype 3R₁ hydroxalcalite (JCPDS 22–700) (10, 11, 13). The in-plane X-ray diffractions from planes (110) and (113) can also be noted at $\sim 60^\circ$ and $\sim 61^\circ$ for these two samples, which reveal a good dispersion of metal ions in the hydroxide layers. Slight differences were observed for samples CoMgAl- and CaCoAl-HTlc compared with MgAl- and CoAl-HTlc, with the corresponding diffraction peaks being weaker. Note that sample MgCaAl-HTlc contains an impure phase CaCO₃ (JCPDS 85–1108, marked with an $\times$ in Figure 1A), while the so-called CaAl-HTlc sample contains a very small portion of the HTlc phase, with CaCO₃ (JCPDS 85–1108) and Al(OH)₃ (JCPDS 77–0250) being the major phases.

Figure 1B describes the XRD patterns of derived mixed oxides, which reveal that the precursor HTlcs were decomposed, leading to the various oxide derivatives. For samples containing Mg but without Co (i.e., MgAlO and MgCaAlO), the periclase (MgO, JCPDS 43–1022) is the major phase, characteristic of three peaks at 37° , 43° , and 62° , with trace amounts of the spinel phase (MgAl₂O₄, JCPDS 21–152) (14) and CaCO₃. For samples containing Co, the oxide is mainly of the spinel phase, with the characteristic diffraction peaks at $\sim 31^\circ$, 36° , 39° , 45° , 55° , 59° , and 65° (Co₂AlO₄, JCPDS 38–0814; CoAl₂O₄, JCPDS 82–2246) (15). These observations suggest that the introduction of Co into the hydroxalcalite promotes formation of the spinel phase after calcination at 550 °C. On the other hand, Ca-containing oxides, such as MgCaAlO and CaAlO, contain the CaCO₃ phase, as marked in Figure 1B. The existence of CaCO₃ in these oxides is further confirmed by infrared spectra (see Figure 1S, Supporting Information).

The BET SSA, pore size, and pore volume of the oxides derived are listed in Table 1. Obviously, the composition severely affects the SSA and pore volume. Except for CaAlO possessing a smaller SSA (26 m²/g) and pore volume (0.09 cm³/g), all other oxides have a relatively high surface area (91–253 m²/g), with a medium-scale pore volume (0.23–0.98 cm³/g). The interparticle pore diameter calculated falls in the range of 9.6–15.4 nm, and thus gas molecule diffusion in the pores should not be the rate-determining step for the subsequent CO₂ adsorption (11).

Thermal Decomposition Behaviors of HTlc Precursors.

Figure 2 presents the weight loss events of these HTlcs during heating in the air. In general, thermogravimetric loss during

FIGURE 1. XRD patterns of (A) prepared HTlcs and (B) oxide sorbents where CaCO_3 was marked as "x", $\text{Al}(\text{OH})_3$ as "#", spinel as "S", periclase as "P", and unknown as "u".

FIGURE 2. DTG profiles of the precursors HTlcs.

heating involves two or three steps. The first step occurs at 50–200 °C, mainly ascribed to the loss of surface-adsorbed and interlayer water molecules (10). The second stage takes place at 200–500 °C, including the dehydroxylation of layer hydroxyl groups and decomposition of interlayer carbonate, causing collapse of the layer structure (10). Note that this event for MgAl-HTlc occurs at 441 °C. When Co replaces partial or all Mg in HTlc, this event takes place at much lower temperatures (337 and 247 °C for CoMgAl- and CoAl-HTlc, respectively). In contrast, the replacement of partial or all Mg with Ca leads to one more event at a much higher temperature (i.e., the third step). For example, samples CaAl- and MgCaAl-HTlc have a weight loss peak at 798 and 749 °C, respectively, attributed to the decomposition of CaCO_3 to CaO (16, 17), as confirmed by the TGA of synthetic CaCO_3 (see Figure 2S, Supporting Information). Such a peak can be marginally noted in sample CaCoAl-HTlc at *ca.* 700 °C. This evidence suggests that the incorporation of Co into the hydroxide layer facilitates the decomposition of HTlc in two aspects. Since $\text{Mg}(\text{OH})_2$ is thermally more stable than $\text{Co}(\text{OH})_2$ (15), which is also reflected by the temperature decrease

from 441 °C (MgAl-HTlc) to 247 °C (CoAl-HTlc) for the second weight loss, Co first destabilizes the hydroxide layers thermally. Second, the Co presence in the system catalytically promotes the decomposition of carbonate because decarbonation likely occurs simultaneously with dehydroxylation, and there is no other weight loss peak corresponding to CO_2 release in these samples. In Ca-containing HTlcs, Ca seemingly also facilitates the dehydroxylation (e.g., 283 and 342 °C for samples CaAl- and MgCaAl-HTlc, respectively) probably due to the lower thermal stability of $\text{Ca}(\text{OH})_2$, but it also delays the decomposition of carbonate in the CaCO_3 form that is either existing in the precursor or freshly formed during dehydroxylation. It is worthy noting that there is only a very weaker band at *ca.* 700 °C for CaCoAl-HTlc; that is, decarbonation mainly takes place in the second step, further suggesting the catalytic activity of Co for decarbonation. Therefore, after calcination at 550 °C, decarbonation would be only partial, and CaCO_3 is still present in MgCaAlO and CaAlO, which would have a negative impact on their CO_2 sorption capability, as addressed shortly.

CO_2 Adsorption on the Oxide Sorbents. The typical adsorption breakthrough curves of CO_2 over the oxide sorbents are presented in Figure 3, and the curves of three other oxide sorbents are provided in Figure 3S of the Supporting Information. All oxide sorbents seemingly follow a similar sorption pattern. As shown in Figure 3, CO_2 was completely adsorbed in the initial stage (3–4 min), as no CO_2 was detected in the outlet stream. Afterward, the CO_2 concentration gradually increases to the feeding level in the next 10–15 min. This has been reflected by the gradual increase of the $C_{\text{CO}_2,\text{out}}/C_{\text{CO}_2,\text{in}}$ ratio ($C_{\text{CO}_2,\text{out}}$ and $C_{\text{CO}_2,\text{in}}$ refer to the CO_2 concentrations in the outlet and inlet N_2 stream, respectively) from 0 to 1 (Figure 3). The $C_{\text{CO}_2,\text{out}}/C_{\text{CO}_2,\text{in}}$ ratio is much more quickly recovered to 1 when there is no sorbent placed in the reactor (small-dot curve in Figure 3). In comparison, oxide CaCoAlO captures more CO_2 at 350 °C than the other oxides. The capture amount, 1.39 mmol/g, that is, 6.12 wt %, was estimated by integrating the area between the simulated sorption curve (filled-square curve, addressed shortly) and the blank curve (small-dot curve). The estimation accuracy was confirmed by the weight gain (6.22 wt % for CaCoAlO and 4.90 wt % for MgAlO) in TGA using 8% CO_2 in N_2 flowing for 18 h at 350 °C (see Figure 4S, Supporting Information).

FIGURE 3. CO₂ sorption data in the fixed-bed reactor and simulated breakthrough curves of some oxides. "M-" represents predicated curves.

TABLE 2. Performance Summary of HTlc-Derived Sorbents Capturing CO₂

sorbent	sorption temperature (°C)	feeding composition and pressure O ₂ proportion	capture amount (mmol/g)	ref
CaCoAlO	350	8% CO ₂ , 1 atm	1.39	this work
MgAlO	350	8% CO ₂ , 1 atm	1.13	this work
MgAl-HT	300	pure CO ₂ , 1 bar	0.5	ref 6
MgAl-HT-400	300	pure CO ₂ , 100 kPa	0.249	ref 7
MgAl-HT-550	400	15% CO ₂ , 1 atm	1.18	ref 8
MgAl-HT coatings	300	pure CO ₂ , 1 atm	~1.0	ref 9
K ₂ CO ₃ promoted MgAl-HT	400	3% CO ₂ , 10 atm	0.9	ref 6

Table 1 lists the CO₂ sorption amounts of all oxides. Note that, in the binary oxides, the capture capacity of MgAlO (1.13 mmol/g, i.e., 4.97 wt %) is higher than those of CaAlO (0.87 mmol/g) and CoAlO (1.03 mmol/g). It is our belief that two factors, that is, the active site and CO₂ affinity of the oxide sorbent, are determinant. It is well-known that CaO can quickly capture and strongly hold CO₂ in the carbonate form (highest sorption affinity for CO₂), so CaAlO should possess the highest sorption capacity. However, as mentioned previously (Figures 1B and 2), CaAlO contains some CaCO₃, so the active sites (CaO-like) available for adsorbing CO₂ in CaAlO are much fewer, resulting in a lower capture capacity. CoAlO, on the other hand, possesses the lowest CO₂ affinity, or say the adsorbed CO₂ in carbonate form is easily decomposed by the catalytic Co component, thus also leading to a lower capture amount. MgAlO, in between these two "extreme" cases but with a high surface area (Table 1), captures more CO₂ under the same conditions. In the tertiary oxides, trading off between the CO₂ affinity and the active sites makes sample CaCoAlO capture the highest amount of CO₂ (1.39 mmol/g). In comparison with MgAl-HTlc and the derived oxides reported elsewhere (Table 2) (6–9), the CO₂ capture amount by CaCoAlO is the highest under similar conditions.

Compared with other inorganic sorbents, such as zeolites and Li₂ZrO₃, our CaCoAlO and MgCoAlO oxides also show some advantages. It is true that ASRT 5A, as an example of zeolites, can adsorb 3–4 mmol/g (13–17 wt %) of CO₂ at 0–50 °C. However, its CO₂ sorption capacity suddenly decreases

to 1.43 wt % at 250 °C (18). In contrast, our oxides can take up 5–6 wt % at 350 °C, and their sorption capacity is only slightly decreased at 400–500 °C (9). On the other hand, HTlc-derived oxides can be readily prepared at low temperatures (550 °C) for 4 h, while Li₂ZrO₃ has to be prepared at 850–1000 °C for 12 h, so that the preparation cost may be higher even though it can adsorb up to 20 wt% of CO₂ at 500 °C (19).

Modeling of CO₂ Adsorption on Mixed Oxides. CO₂ adsorption on these oxides is more likely a chemisorption, involving a number of steps, such as CO₂ diffusing into the surface and pores, reacting with the active sites, and forming a product layer on the surface in the carbonate form. With the sorption going on, it becomes more difficult for CO₂ to diffuse into the innerpores/surface or penetrate the product layer to be adsorbed. It seems that the sorbent is gradually deactivated, and the relevant gas–solid sorption process can be described with the deactivation model, as already used for CO₂ sorption on calcined HTlcs (8) and for the sorption of SO₂, H₂S, and so forth on various solid materials (20, 21). In this model, an activity term *a* is introduced into the rate expression to represent the deactivation due to a decrease of the active site concentration and the textural changes and so forth. Assuming the pseudo-steady-state adsorption and neglecting the axial dispersion term, one can express the species conservation equation for CO₂ concentration and the rate equation for the activity change of the solid reactant with respect to time as eqs 1 and 2:

$$-Q \frac{dC_A}{dW} - \kappa_0 C_A a = 0 \quad (1)$$

$$-\frac{da}{dt} = \kappa_d C_A^n a^m \quad (2)$$

where *C_A* is the CO₂ concentration in the outlet stream, *a* is the activity of the oxide sorbent, *κ₀* is the initial sorption rate constant (cubic centimeters per minute gram) and *κ_d* is the deactivation rate constant (per minute), *W* is the sorbent mass (grams), and *Q* is volumetric flow rate (cubic centimeters per minute).

Normally, the deactivation rate is expected to depend on CO₂ concentration, so the solution of this model gives the following equation for the breakthrough curve (taking *n* = *m* = 1):

$$\frac{C_A}{C_{A_0}} = \exp \left[\frac{\{1 - \exp[(\kappa_0 W/Q)(1 - \exp(-\kappa_d t))]\}}{[1 - \exp(-\kappa_d t)]} \exp(-\kappa_d t) \right] \quad (3)$$

The regression analysis of the experimental breakthrough data obtained for CO₂ sorption on our oxide sorbents resulted in two parameters: *κ₀* and *κ_d*, as listed in Table 1. The regression seems very good, as the correlation coefficient *R*² is more than 0.98 in all cases. The prediction using the as-obtained breakthrough equation is in good agreement with the experimental data (Figure 3). For all sorbents except for CaCoAlO, both the initial sorption rate constant *κ₀* and the deactivation rate constant *κ_d* are quite similar, with the average values of *κ₀* and *κ_d* being 165 cm³/min g and 0.57 min^{−1}, respectively. However, the constant *κ₀* of oxide CaCoAlO (212 cm³/min g) is much larger than the average (165 cm³/min g), being consistent with its highest sorption capacity for CO₂.

Species Formed on Oxide Sorbents. The adsorbed species formed from CO₂ on the oxide sorbent can be identified by *in situ* IR spectra. As shown in Figure 4 for sample CoCaAlO, the time-dependent IR spectra indicate that various vibrational peaks, corresponding to the chemisorbed CO₂ species, are gradually intensified with time during the sorption at 350 °C. After 20 min, their intensities are no longer increased, revealing that CO₂ sorption reaches the steady state after 20

FIGURE 4. Time-frame *in situ* IR spectra of CO₂ sorption on CaCoAlO at 350 °C.

min. The vibrational peaks in the spectra demonstrate that various forms of carbonates are formed during the adsorption. For example, monodentate carbonate can be identified by the peaks at 1426, 1337, and 1042 cm⁻¹ and bicarbonate by the peak at 1229 cm⁻¹ and the shoulders at 1600 (especially at 5 min) and 1520 cm⁻¹ (22). The strong broad peak at 1578–1589 cm⁻¹ could be attributed to monodentate and bidentate carbonates (22), and the bridged carbonate could be recognized by the weak peak at 1782–1786 cm⁻¹ as well. The vibrational frequencies and their assignments are summarized in Table 5S of the Supporting Information (23, 24). These various forms of carbonates are mainly associated with Ca, as unveiled by the differential thermogravimetry (DTG) profile (see Figure 2S, Supporting Information). In this profile, a weight loss at 779 °C is only attributed to the decomposition of CaCO₃-like material.

In conclusion, various well-mixed oxides derived from the corresponding HTLCs show relatively high CO₂ sorption capacity at 350 °C. In particular, our oxide CaCoAlO can adsorb 1.39 mmol/g, that is, 6.12 wt %, of CO₂ at 350 °C within 20 min, indicating a promising cost-effective CO₂ adsorbent.

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Supporting Information Available

FTIR spectra of some oxides and HTLC for CaCO₃ identification, DTG profiles of synthetic CaCO₃ and CaCoAlO adsorbing CO₂, breakthrough curves of some other oxide sorbents, weight gain profiles of CaCoAlO and MgAlO in TGA, assignment of bands to various carbonate species. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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