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

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Various $X_nY_{3-x}Al$-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 $X_nY_{3-x}AlO$ 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 $M_{x+y}^+M_{2-x-y}^{2+}[OH]_x$,$\cdot$$nH_2O$ ($x=0.2–0.4$), where $M^+$ and $M^{2+}$ 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$_3$ 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$_x$Co$_y$Ca$_z$Al$_{(x+y+z)}$ ($x+y+z=3$) HTlcs were synthesized using the coprecipitation method (denoted as Mg$_x$Co$_y$Ca$_z$Al-HTlc). First of all, a mixed salt solution (150 mL) containing a stoichiometric atomic ratio (Table 1) of Ca(NO$_3$)$_2$·4H$_2$O (>99%, Yili company), Co(NO$_3$)$_2$·6H$_2$O (>99%, Jinke company), Mg(NO$_3$)$_2$·6H$_2$O (>99%, Yili company), and Al(NO$_3$)$_3$·9H$_2$O (>99%, Yili company), and a solution (150 mL) of NaOH (>96%, Beihua company) and Na$_2$CO$_3$ (>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.
and Simulated Parameters of Oxide Sorbents

with the above method, we used TGA to determine the direct

$\text{CO}_2$ absorption amount was further calculated from the $\text{CO}_2$ concentration in the outlet

was thus calculated by integrating the GC peak area. The
detected from $\text{N}_2$ to $\text{CO}_2/N_2$ gas mixture at 350

was passed through the fixed bed. The space velocity was

from CaCO$_3$ (JCPDS 85–1108, marked with an

Figure 1B describes the XRD patterns of derived mixed

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 hydrotalcite. The peaks at $2\theta \approx 11^\circ$, 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 $\sim 35^\circ$, $38^\circ$, and $46^\circ$ attributed to (012), (015), and (018) crystal planes are characteristic of polytype 3R, hydrotalcite (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 $\sim 64^\circ$ 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 CaCO$_3$ (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 CaCO$_3$ (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 (MgAl$_2$O$_4$, JCPDS 21–152) (1/4) and CaCO$_3$. 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° (CoAlO$_4$, JCPDS 88–0814; CoAl$_2$O$_4$, JCPDS 82–2246) (15). These observations suggest that the introduction of Co into the hydrotalcite promotes formation of the spinel phase after calcination at 550 °C. On the other hand, Ca-containing oxides, such as MgCaAlO and CaCoAlO, contain the CaCO$_3$ phase, as marked in Figure 1B. The existence of CaCO$_3$ 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 m$^2$/g) and pore volume (0.09 cm$^3$/g), all other oxides have a relatively high surface area (91–253 m$^2$/g), with a medium-scale pore volume (0.23–0.98 cm$^3$/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 CO$_2$ 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

| TABLE 1. Composition, Textural Property, $\text{CO}_2$ 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) | $k_a$ (cm$^3$/g min) | $k_d$ (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           | 0.08           | 0.87             | 163.2           | 0.59          |
| CoMgAlO         | 1.5:1:1:1   | 127            | 14.1           | 0.45           | 1.05             | 170.3           | 0.63          |
| MgCaAlO         | 2:1:1:1     | 253            | 15.4           | 0.98           | 1.28             | 180.6           | 0.54          |
| CaCoAlO         | 1.5:1:1:1   | 91             | 10.6           | 0.24           | 1.39             | 212.5           | 0.55          |

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 ($\sim 50$ 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 Harrick series 999 temperature controller was used to control the experimental temperature. Prior to the IR spectrum recording, the oxide sample was flushed with pure $\text{N}_2$ 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% $\text{CO}_2$ in $\text{N}_2$ was introduced at 25 mL/min for $\text{CO}_2$ 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 hydrotalcite. The peaks at $2\theta = 11^\circ$, 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 $\sim 35^\circ$, $38^\circ$, and $46^\circ$ attributed to (012), (015), and (018) crystal planes are characteristic of polytype 3R, hydrotalcite (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 CaCO$_3$ (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 CaCO$_3$ (JCPDS 85–1108) and Al(OH)$_3$ (JCPDS 77–0250) being the major phases.
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 samples 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 CaCO₃ to CaO (16, 17), as confirmed by the TGA of synthetic CaCO₃ (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 Mg(OH)₂ is thermally more stable than Co(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 CO₂ 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 Ca(OH)₂, but it also delays the decomposition of carbonate in the CaCO₃ 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 CaCO₃ is still present in MgCaAlO and CaAlO, which would have a negative impact on their CO₂ sorption capability, as addressed shortly.

CO₂ Adsorption on the Oxide Sorbents. The typical adsorption breakthrough curves of CO₂ 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, CO₂ was completely adsorbed in the initial stage (3–4 min), as no CO₂ was detected in the outlet stream. Afterward, the CO₂ concentration gradually increases to the feeding level in the next 10–15 min. This has been reflected by the gradual increase of the C_CO₂,out/C_CO₂,in ratio (C_CO₂,out and C_CO₂,in refer to the CO₂ concentrations in the outlet and inlet N₂ stream, respectively) from 0 to 1 (Figure 3). The C_CO₂,out/C_CO₂,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 CO₂ 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% CO₂ in N₂ flowing for 18 h at 350 °C (see Figure 4S, Supporting Information).
zeolites, can adsorb 3–4 mmol/g (13–17 wt %) of CO2 at 0–50 °C. 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. MgAl-HT coatings promote MgAl-HT 400 3% CO2, 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 two factors, that is, the active site and CO2 affinity of the oxide sorbent, are determinant. It is well-known that CaO (0.87 mmol/g) and CoAlO (1.03 mmol/g). It is our belief that, in the binary oxides, the capture capacity of MgAlO is much fewer, resulting in a lower capture capacity.

Figure 3 shows the CO2 sorption data in the fixed-bed reactor and simulated breakthrough curves of some oxides. "M-" represents precipitated MgAlO, "M-CoMgAlO" represents MgCoMgAlO, and "M-CoCaAlO" represents CaCoMgAlO. The performance summary of HTlc-derived sorbents of CO2 capture is tabulated in Table 2.

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

<table>
<thead>
<tr>
<th>sorbent</th>
<th>sorption temperature (°C)</th>
<th>feeding composition and pressure (O2 proportion)</th>
<th>capture amount (mmol/g)</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCoAlO</td>
<td>350</td>
<td>8% CO2, 1 atm</td>
<td>1.39</td>
<td>this work</td>
</tr>
<tr>
<td>MgAlO</td>
<td>350</td>
<td>8% CO2, 1 atm</td>
<td>1.13</td>
<td>this work</td>
</tr>
<tr>
<td>MgAl-HT</td>
<td>300</td>
<td>pure CO2, 1 bar</td>
<td>0.5</td>
<td>ref 6</td>
</tr>
<tr>
<td>MgAl-HT-400</td>
<td>300</td>
<td>pure CO2, 100 kPa</td>
<td>0.249</td>
<td>ref 7</td>
</tr>
<tr>
<td>MgAl-HT-550</td>
<td>400</td>
<td>15% CO2, 1 atm</td>
<td>1.18</td>
<td>ref 8</td>
</tr>
<tr>
<td>MgAl-HT</td>
<td>300</td>
<td>pure CO2, 1 atm</td>
<td>~1.0</td>
<td>ref 9</td>
</tr>
<tr>
<td>K2CO3 coatings</td>
<td>300</td>
<td>pure CO2, 1 atm</td>
<td>~1.0</td>
<td>ref 9</td>
</tr>
<tr>
<td>MgAl-HT</td>
<td>400</td>
<td>3% CO2, 10 atm</td>
<td>0.9</td>
<td>ref 6</td>
</tr>
</tbody>
</table>

The regression analysis of the experimental breakthrough data obtained for CO2 sorption on our oxide sorbents resulted in two parameters: k0 and kδ, 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 k0 and the deactivation rate constant kδ are quite similar, with the average values of k0 and kδ being 165 cm3/min g and 0.57 min−1, respectively. However, the constant k0 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
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$^{-1}$ as well. Various forms of carbonates are mainly associated with Ca, as unveiled by the differential thermogravimetry (DTG) profile (see Figure 2S, Supporting Information).

The vibrational frequencies and their assignments are summarized in Table 5S of the Supporting Information. For example, monodentate carbonate can be identified by the weak peak at 1782–1786 cm$^{-1}$ as well. Various forms of carbonates are mainly associated with Ca, as unveiled by the differential thermogravimetry (DTG) profile (see Figure 2S, Supporting Information).

In conclusion, various well-mixed oxides derived from Ca 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 CaCO$_3$-like material.

Acknowledgments
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Supporting Information Available
FTIR spectra of some oxides and HTLC for CaCO$_3$ identification, DTG profiles of synthetic CaCO$_3$ and CaCOAlO adsorbing CO$_2$, 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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