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# Markedly Improved $CO_2$ Capture Efficiency and Stability of Gallium Substituted Hydrotalcites at Elevated Temperatures

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Forty percent of all carbon dioxide emissions are attributed to burning fossil fuels (coal, natural gas, oil) for power generation.[1,2] $CO_2$ emissions from such sources are expected to double current emissions owing to the construction of new coal-fired power plants, ~100 per year for the next 25 years.[3] The global carbon cycle currently is unbalanced by 3.2 gigatons of excess $CO_2$;[4] therefore, it is essential to capture most carbon dioxide emitting from such current and future stationary sources. Unfortunately, known $CO_2$ sorbents for these applications suffer either from early depletion or from large energy requirements for regeneration[2] and, if installed, would also bring an 8−35% energy penalty.[5−7] Moreover, $CO_2$ from hot gas streams, such as exhaust from fossil fuel based power plants,[8,9] requires robust materials that either operate or are stable at elevated temperatures.[10,11]

Hydrotalcites (HTs) belong to a family of layered, double hydroxide solids that have been proven to be stable adsorbents under harsh conditions.[12] The stoichiometry[13,14] of these solids is

$$M^{2+}_{1-x}M^{3+}_{x}(OH)_2A^{m-}_{x/m}\cdot yH_2O$$

where the divalent ion is typically $Mg^{2+}$, the trivalent ion is typically $Al^{3+}$, and the anion A is $Cl^-$, $NO_3{}^-$, or $CO_3{}^{2-}$. Although important members of this family containing $Ga^{3+}$ substituted for some fraction of the $Al^{3+}$ have been synthesized,[15,16] there are no existing reports of $CO_2$ capture by these substituted hydrotalcites (SHTs). Here we report stable and reversible $CO_2$ adsorbents with very high capture capacity that feature Ga substituted, potassium carbonate promoted HTs:

$$CO_2+\text{calcined-SHT} \underset{400°C}{\overset{200°C}{\rightleftharpoons}} \text{calcined-SHT}(CO_2)$$

In a typical synthesis, gallium (10 mol % substituted for Al) substituted hydrotalcites (Ga-SHT, Figure 1) were prepared by a procedure slightly modified from the conventional hydrotalcite synthesis (see Supporting Information).[17] In addition, Ga-SHT was further customized by stirring a 1 g portion of the material in 50 mL of water containing 2.0 M potassium carbonate for 2 h before removing the water at 70 °C under a slight vacuum.

The SHTs were then converted into the respective $CO_2$ adsorbents by calcining at 400 °C in an inert gas atmosphere. The $CO_2$ adsorption experiments were conducted at 200 °C, and the $CO_2$ partial pressure was 0.7 atm. The $CO_2$ adsorption capacities were obtained using a thermal gravimetric apparatus (TGA) to measure weight gain under a "dry" gas stream containing $CO_2$ (about 0.7 atm partial pressure) and an inert gas. The results for unsubstituted calcined HT, calcined Ga-SHT, and $K_2CO_3$-promoted calcined HT and calcined Ga-SHT are summarized in Table 1. In such experiments, both $K_2CO_3$-promoted calcined HT and calcined Ga-SHT demonstrated an adsorption capacity of 1.3 mmol of $CO_2$ adsorbed per gram of adsorbent. This is comparable to the industrial standard for $CO_2$ removal, monoethanol amine (MEA) at 1.36 mmol/g.[18] These data also show that exchanging the HTs with potassium carbonate leads to calcined materials with about three-fold increased

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(1) Schrag, D. P. *Science* **2007**, *315*, 812–813.
(2) Yang, H. Q.; Xu, Z. H.; Fan, M. H.; Gupta, R.; Slimane, R. B.; Bland, A. E.; Wright, I. *J. Environ. Sci. China* **2008**, *20*, 14–27.
(3) Rau, G. H.; Caldeira, K. *Science* **2007**, *316*, 691–691.
(4) Metz, B.; Davidson, O.; de Coninck, H.; Loos, M.; Meyer, L. IPCC Special Report on Carbon Dioxide Capture and Storage; Cambridge University Press: New York, NY, 2005.
(5) Halmann, M. M.; Steinberg, M. Greenhouse Gas Carbon Dioxide Mitigation: Science and Technology; Lewis Publishers: Boca Raton, 1999.
(6) Gupta, H.; Fan, L. S. *Ind. Eng. Chem. Res.* **2002**, *41*, 4035–4042.
(7) Yeh, J. T.; Resnik, K. P.; Rygle, K.; Pennline, H. W. *Fuel Process. Technol.* **2005**, *86*, 1533–1546.
(8) Feng, B.; An, H.; Tan, E. *Energy Fuels* **2007**, *21*, 426–434.
(9) Yong, Z.; Mata, V.; Rodrigues, A. E. *Sep. Purif. Technol.* **2002**, *26*, 195–205.
(10) Abanades, J. C.; Rubin, E. S.; Anthony, E. J. *Ind. Eng. Chem. Res.* **2004**, *43*, 3462–3466.
(11) Yong, Z.; Mata, V.; Rodrigues, A. E. *Ind. Eng. Chem. Res.* **2001**, *40*, 204–209.
(12) Hufton, J. R.; Mayorga, S.; Sircar, S. *AIChE J.* **1999**, *45*, 248–256.
(13) Miyata, S. *Clays Clay Minerals* **1983**, *31*, 305–311.
(14) Taylor, H. F. W. *Mineralogical Magazine* **1973**, *39*, 377–389.
(15) Bellotto, M.; Rebours, B.; Clause, O.; Lynch, J.; Bazin, D.; Elkaim, E. *J. Phys. Chem. A* **1996**, *100*, 8535–8542.
(16) Rousselot, I.; Gueho-Taviot, C.; Besse, J. P. *Int. J. Inorg. Mater.* **1999**, *1*, 165–174.
(17) White, M. G.; Iretski, A. V.; Weigel, S. J.; Chiang, R. L.; Brzozowski, J. R. U.S. Patent 7,442,232, October 28, **2008**.
(18) Gupta, H.; Fan, L. S. *Ind. Eng. Chem. Res.* **2002**, *41*, 4035–4042.

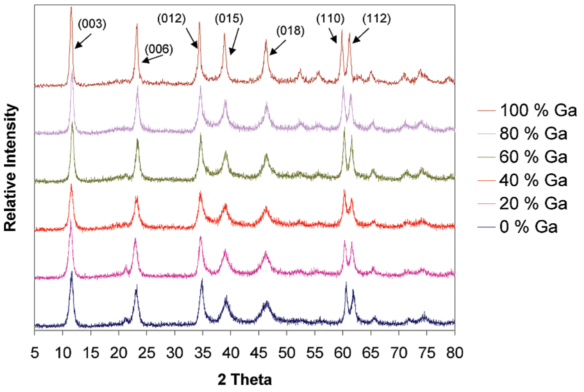

**Figure 1.** Powder X-ray diffraction (PXRD) patterns of layered double hydroxide containing gallium and aluminum. From top to bottom: $Mg_6Al_{2(1-x)}Ga_{2x}(OH)_{16}CO_3 \cdot xH_2O$, $x = 1$; 0.8; 0.6; 0.4; 0.2; 0.

**Table 1. $CO_2$ Reversible Sorption Capacities under Cyclic Temperature Swing Operations**

| | | mmoles $CO_2$/g hydrotalcite | | |
|---|---|---|---|---|
| no. | sample | cycle 1 | cycle 2 | cycle 3 |
| 1 | unpromoted 0% Ga | 0.099 | 0.058 | |
| 2 | unpromoted 10% Ga | 0.17 | 0.16 | 0.143 |
| 3 | $K_2CO_3$-promoted 0% Ga | 0.57 | 0.52 | |
| 4 | $K_2CO_3$-promoted 10% Ga | 0.58 | 0.57 | 0.55 |

**Table 2. Carbon Dioxide Adsorption Capacity for Calcined Gallium Substituted Hydrotalcites (Ga-SHT)**

| adsorbent | $CO_2$ capacity (mmol/g) | Ga/(Ga+Mg+Al) |
|---|---|---|
| 0% Ga-SHT | 0.440 | 0 |
| **5% Ga-SHT** | **0.570** | **0.013** |
| 10% Ga-SHT | 0.531 | 0.035 |
| 0% Ga-SHT, with $K_2CO_3$ | 0.467 | 0 |
| 1% Ga-SHT, with $K_2CO_3$ | 0.97 | 0.0022 |
| 5% Ga-SHT, with $K_2CO_3$ | 1.122 | 0.013 |
| **10% Ga-SHT, with $K_2CO_3$** | **1.400** | **0.035** |
| 20% Ga-SHT, with $K_2CO_3$ | 0.69 | 0.049 |
| 30% Ga-SHT, with $K_2CO_3$ | 0.74 | 0.074 |
| 40% Ga-SHT, with $K_2CO_3$ | 0.55 | 0.111 |
| 50% Ga-SHT, with $K_2CO_3$ | 0.54 | 0.126 |
| 60% Ga-SHT, with $K_2CO_3$ | 0.50 | 0.167 |
| 80% Ga-SHT, with $K_2CO_3$ | 0.43 | 0.226 |
| 90% Ga-SHT, with $K_2CO_3$ | 0.45 | 0.252 |

capacity for adsorbing $CO_2$ from the gas streams at 200 °C.

The resulting $K_2CO_3$-promoted calcined Ga-SHT-($CO_2$) adduct displayed a $CO_2$ desorption rate of 0.22 $min^{-1}$ at 400 °C, indicating a first order process. These materials were subjected to several $CO_2$ adsorption/desorption cycles by swinging the temperature from 200 to 400 °C and back. The Ga substituted materials proved to be the more robust, maintaining their activity of $CO_2$ adsorption through at least three cycles. Through controlled studies, 10% Ga substitution was found to be best (Table 2).

To study the effects of gallium content and potassium carbonate promotion on the kinetics of reconstruction at ambient conditions, powder X-ray diffraction (PXRD) patterns were collected of the calcined samples after repeated cycles of calcination and reconstruction at ambient conditions. It is also known that structural deformation occurs when oxides and spinels appear at elevated temperatures.[19] In Figure 2, PXRD spectra of Ga-SHT after three cycles are shown. The hydrotalcite framework is substantially preserved even after three calcinations and reconstructions. Also, desorption and decomposition (DTG) profiles (Figures S1 and S2, Supporting Information) show narrow differences between cycles for SHTs.

To better understand the structural integrity of the SHTs, we must first examine them in more detail. They consist of positively charged brucite structures, $Mg(OH)_2$, separated by intercalated anions[20,21] in a hexagonal unit cell for which $a = b$, where $a$ increases as the gallium fraction increases.[15] Figure 1 shows X-ray diffraction data for the Ga exchanged ($Mg_6Al_{2(1-x)}Ga_{2x}(OH)_{16}CO_3 \cdot xH_2O$ where $x = 0-1.0$) carbonated form of the layered double hydroxides with the assignment of the Miller indices to the peaks. There is a systematic shift and sharpening of the Bragg diffraction peaks as Ga replaces Al, for example, the reflection near 12° (003) and the peaks at 58−62° (110) (Figure 3). These more-highly exchanged samples also demonstrate faster reconstruction kinetics when the calcined solids were contacted with moist air to regenerate the SHT from the calcined solid (see Figures S3−S6 for representative PXRD spectra on regenerated SHTs and Table S1 for respective chemical compositions of SHTs, Supporting Information).

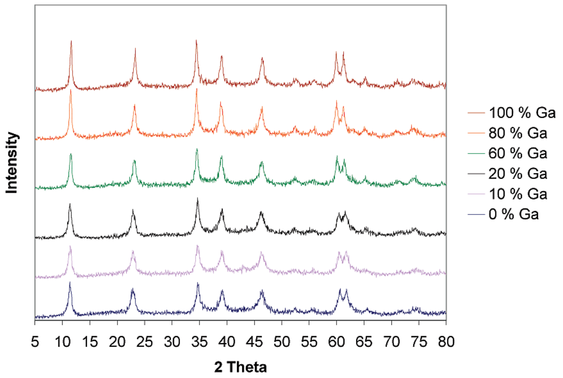

**Figure 2.** PXRD scans of LDHs after three calcinings and exposure to atmospheric conditions. 0% Ga substitution (dark blue curve); 10% Ga substitution (purple curve); 20% Ga substitution (black curve); 60% Ga substitution (green curve); 80% Ga substitution (orange curve); 100% Ga substitution (maroon curve).

The $a$ unit cell values of the samples back-exchanged with carbonate anions describe a single curve when correlated by the average cation radius that increases with increasing amounts of Ga substitution (Figure S7, Supporting Information). The PXRD data and anion exchange capacity suggest that a large fraction of the $Ga^{3+}$ in these solids has replaced $Al^{3+}$ in the cationic layer, especially for those solids where the substituted fraction, $x$, is relatively small (~0.05). The $c$-axis parameter for the back exchanged materials (Figure S8, Supporting Information) also showed systematic increases in the value of $2\theta$ as Ga replaces the Al cations.

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(19) Sampieri, A.; Lima, E. *Langmuir* **2009**, *25*, 3634–3639.
(20) Allmann, R. *Acta Crystallogr., Sect. B* **1968**, *24*, 972–977.
(21) Bish, D. L. *Bull. Mineralogie* **1980**, *103*, 170–175.

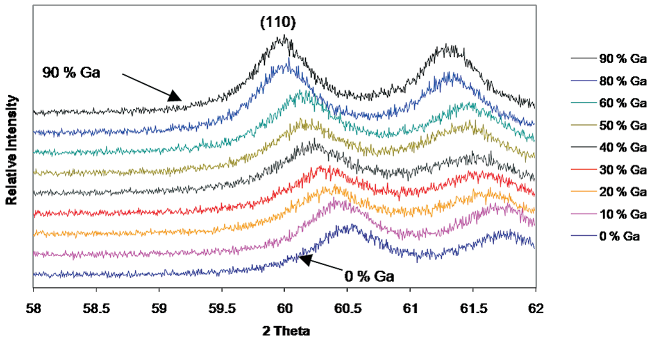

**Figure 3.** Detailed PXRD patterns of layered double hydroxide containing gallium and aluminum to reveal changes in the reflections characteristic of the "a" unit cell parameter. From top to bottom: $Mg_6Al_{2(1-x)}$-$Ga_{2x}(OH)_{16}CO_3 \cdot xH_2O$, $x = 0.9$; 0.8; 0.6; 0.5; 0.4; 0.3; 0.2; 0.1; 0.

Larger crystallite sizes are evident from the sharpening of the peaks for the samples that are richer in Ga than Al. The cationic layers expand in a manner suggested by Vegard's rule,[22,23] as shown by the decrease in the angles of the (110) reflections (Figure 3). It is known that the carbonate anions arrange in a fashion where the $C_3$ rotation axis is perpendicular to the metal oxide layers. Apparently, the samples back-exchanged with carbonate anion have spacings between the layers that do not depend *directly* upon the nature of the reagents to prepare the hydrotalcites; however, the spacing does depend upon the (Ga + Al)/Mg ratio, which is regulated by the type of anion used to prepare them (Figure S9, Supporting Information).

Addition of $K_2CO_3$ (~0.13 wt % reported as $K_2O$) causes the *c*-unit cell parameter to contract by 0.15 to 0.20 Å, whereas the *a*-unit cell parameter is unchanged. This result suggests that $K^+$ must reside in the galleries between the cationic layers and thereby influence unit cells' volume. Potassium ions form hydrates, thereby decreasing the volume of the interlayer water. PXRD data are consistent with $K^+$ forming tightly compacted hydrates without changing the structure of the cationic layer and thus leaving the *a*-unit cell parameters unchanged.

The surface areas of the samples decreased for increasing amounts of Ga in the structure from 86 to 50 $m^2/g$ (Table S2, Supporting Information). A layered double hydroxide[15] with neither Ga nor K showed a surface area of 40 $m^2/g$, suggesting that the $K_2CO_3$ treatment improved the specific surface area significantly.

From the results described here, we conclude that gallium substitution reinforces the layered structure and increases $CO_2$ adsorptivity and stability through multiple cycles when compared to unsubstituted hydrotalcites. The increase in the $d_{440}$ spacing upon potassium carbonate promotion also suggests that potassium is incorporated into the periclase-like phase and that, upon repeated calcining and reconstruction cycles, the potassium carbonate may be migrating out of the periclase-like structure.

Temperature and pressure controlled testing indicates that these SHTs maintain their abilities to adsorb $CO_2$ even in gas mixtures including water vapor, hydrocarbons (naphtha, methane, ethane, and ethene), carbon monoxide, hydrogen ($H_2$), nitrogen ($N_2$), and oxygen ($O_2$). The temperature of the adsorption zone for cyclic adsorption processes was kept in the range of 100 to 160 °C, when $CO_2$ is being separated from hydrocarbons such as alkanes or alkenes. For these temperature swing adsorption (TSA) processes, the adsorbent regeneration temperature was maintained in the range of 350 to 400 °C. For pressure swing adsorption (PSA) processes, the pressure in the adsorption zone was in the range of 5−10 atm, while in the desorption zone it was maintained in between 0.1 and 0.3 atm. Further data will be presented in future publications.

In summary, this report demonstrates that substituted hydrotalcites are viable options as efficient and selective $CO_2$ sorbents in the presence of other components in the gas stream including water, hydrocarbons, and carbon monoxide. Promotion with potassium carbonate tripled the $CO_2$ capture capacities, and $Ga^{3+}$ substitution made the superstructure robust and stable at elevated temperatures for repetitive applications.

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**Supporting Information Available:** Detailed synthesis of substituted hydrotalcites, temperature programmed desorption (Figure S1), differential thermal gravimetry (Figure S2), PXRD spectra during calcination and reconstructions (Figures S3−S6), chemical composition of SHTs (Table S1), unit cell parameters as a function of average cation radius (Figure S7), surface area of various LDHs before and after calcining (Table S2), (003) reflections of layered double hydroxides derived from chloride precursors (Figure S8), and *c*-spacing parameter vs (Ga + Al)/(Mg) (Figure S9) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(22) Tichit, D.; Bennani, M. N.; Figueras, F.; Ruiz, J. R. *Langmuir* **1998**, *14*, 2086–2091.

(23) Cavani, F.; Trifiro, F.; Vaccari, A. *Catal. Today* **1991**, *11*, 173–301.