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High CO_2 Storage Capacity in Alkali-Promoted Hydrotalcite-Based Material: In Situ Detection of Reversible Formation of Magnesium Carbonate

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Abstract: Alkali-promoted hydrotalcite-based materials showed very high CO_2 storage capacity, exceeding 15 mmol g^{-1} when the carbonation reaction was carried out at relatively high temperature (300–500 °C) and high partial pressure of steam and CO_2. In situ XRD experiments have allowed correlation of high CO_2 capacity to the transformation of magnesium oxide centres into magnesium carbonate in alkali-promoted hydrotalcite-based material. Moreover, it has been clearly shown that crystalline magnesium carbonate may be reversibly formed at temperatures above 300 °C in the presence of sufficient partial pressure of steam in the gas phase, conditions that are prevalent in pre-combustion CO_2 capture. The role of steam appears to be of utmost importance for the formation of the bulk carbonate phase and for its reversibility. It is proposed that a high partial pressure of steam keeps the magnesium oxide periclase phase sufficiently hydroxylated to allow magnesium carbonate formation if a relatively high partial pressure CO_2 is present in the gas phase.

Keywords: carbon storage · gas–solid reactions · layered double hydroxides · solid-state reactions · X-ray diffraction

Introduction

Layered double hydroxides, such as hydrotalcite $Mg_{(1-x)}Al_x(OH)_2(CO_3)_{(x/2)}\cdot nH_2O$, are solid inorganic materials that find numerous applications as antacids, anion exchangers, adsorbents, and catalyst support precursors.[1] The use of these materials in catalytic and adsorption processes at high temperatures is very attractive because both their acid–base and redox properties can be tuned by controlled modification of their chemical composition.[2,3] On the one hand, dehydration, dehydroxylation and decarbonation of layered double hydroxides by thermal treatment lead to the formation of mixed magnesium aluminium oxides with strongly basic properties and suitable mechanical strength for industrial applications; the basicity of these materials can be further controlled by adjusting the Mg/Al ratio and promotion with alkaline cations. On the other hand, partial substitution of Al or Mg by transition metals allows their catalytic activity to be tailored for targeted chemical reactions.

In the chemical industry, hydrotalcite-based materials are very well suited for separation of acidic gases at high temperature.[4–6] These materials are currently being studied for CO_2 capture at the intermediate temperatures (300–500 °C) and relatively high pressures (>25 bar) that are used in the process of hydrogen production.[7–11] In particular, sorption-enhanced water–gas shift (SEWGS) is a technology that is currently at the development stage that can be advantageously used in pre-combustion decarbonisation for CO_2-free electricity production.[12] It combines a high-temperature CO_2 sorbent and a high-temperature water–gas shift catalyst to produce two hot and separate H_2 and CO_2 product streams from syngas. The sorption-enhanced reaction has been demonstrated on the bench scale at 400 °C with a potassium-promoted hydrotalcite-based material with an Mg/Al ratio of 2.9, which combines high CO_2 capture ratio with excellent H_2 purity on the product side.[13] Among other parameters, the cyclic CO_2 uptake capacity of the

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sorbent will impact the size and cost of an industrial facility. Beyond achieving a breakthrough capacity of 1.4 mmol of $CO_2\,g^{-1}$ (stable over hundreds of cycles), the experiments have shown that further CO_2 uptake continued at a much lower rate after breakthrough, so that the final CO_2 sorption capacity of this material could exceed 10 mmol$\,g^{-1}$. Van Selow et al. suggested that magnesium carbonate formation could explain such a high total capacity.[13] Similarly, formation of bulk carbonate species has been proposed by Ritter et al. in modelling studies to describe the reversible adsorption and desorption behaviour of CO_2 in K-promoted hydrotalcite-based materials.[14–16] Although small amounts of magnesium carbonate were previously detected in hydrotalcite-based materials in contact with CO_2,[17] it has never been observed to an extent that would correspond to almost full conversion of magnesium oxide centres in the hydrotalcite-based material to magnesium carbonate. The lack of characterization studies carried out under conditions relevant to SEWGS and industrial gas-separation processes in general explains why such a phenomenon was never reported. However, it is clear that in SEWGS processes under high partial pressures of steam, CO_2 and syngas at a total pressure of about 30 bar, the sorbent should indeed both adsorb and absorb CO_2. In contrast, at lower pressures only the adsorption mechanism is apparent.

Herein we report the results of a rigorous structural study on hydrotalcite-based material under high partial pressures of steam and CO_2, motivated by the development of the SEWGS process in our laboratories. We carried out thermogravimetric experiments to confirm that high CO_2 uptake can be achieved with hydrotalcite-based material at high partial pressures of steam and CO_2. Furthermore, in situ XRD experiments with synchrotron radiation (already recognised as a powerful tool in materials research[18]) were carried out at pressures up to 10 bar and temperatures up to 500 °C at the European Synchrotron Radiation Facility (Swiss-Norwegian Beam Lines, BM01B).

Results and Discussion

Thermal decomposition of hydrotalcite-based material under atmospheric pressure follows a widely accepted pathway. It first consists of a dehydration step corresponding to water removal from the interlayer of the hydrotalcite structure at temperatures between 100 and 200 °C followed by several dehydroxylation and decarbonation steps at temperatures between 300 and 500 °C.[2,19,20] Although the exact temperature at which these processes readily occur depends on several parameters, such as the synthetic preparation method and experimental heat treatment profile, clear structural rearrangements have been generally detected by XRD. After removal of interlayer water, a collapsed layered double hydroxide structure with a reduced basal spacing distance is always observed.[21–23] After dehydroxylation and decarbonation above 350 °C, the layered structure disappears and broad diffraction peaks corresponding to the periclase crystalline phase are usually detected.[24] The significant broadness of the diffraction peaks is often explained by the presence of defects in the periclase structure induced by partial substitution of magnesium by aluminium in the structure, generally described as Mg(Al)O.[25,26] For potassium carbonate promoted hydrotalcite-based materials a similar decomposition pattern under atmospheric pressure has been observed.[27] In contrast, experimental research on SEWGS using a potassium-promoted hydrotalcite-based material for CO_2 adsorption at 350–450 °C and at a total pressure of 30 bar indicated that the magnesium carbonate phase could be generated in significant quantities in the presence of high partial pressures of both steam and carbon dioxide. Formation of $MgCO_3$ has only been indirectly inferred from measurements of CO_2 absorption capacity.[13] Thus, the main goal of this contribution is to validate this reaction pathway at high pressures and temperatures, ex situ and in situ, during carbonation experiments.

Figure 1 shows the XRD pattern of 11 wt % K_2CO_3-promoted hydrotalcite that was subjected to hydrothermal conditions in an autoclave at 350 °C in the presence of high partial pressures of CO_2 and steam, according to the procedure described in the Experimental Section. The presence of a magnesium carbonate crystalline phase suggests that the mixed-oxide periclase Mg(Al)O obtained after heat treatment above 300 °C readily reacted with CO_2 in the presence of steam to give the corresponding carbonated material. Although some previous in situ structural studies carried out in the presence of low partial pressures of CO_2 and low partial pressures of H_2O have revealed only minor formation of a magnesium carbonate phase in co-existence with a periclase Mg(Al)O phase at temperatures close to 350 °C, the XRD pattern of Figure 1 shows only magnesium carbonate crystalline phase. This experiment carried out at high pressure clearly indicates that high partial pressures of CO_2 and steam favour the carbonation reaction rather than the pro-

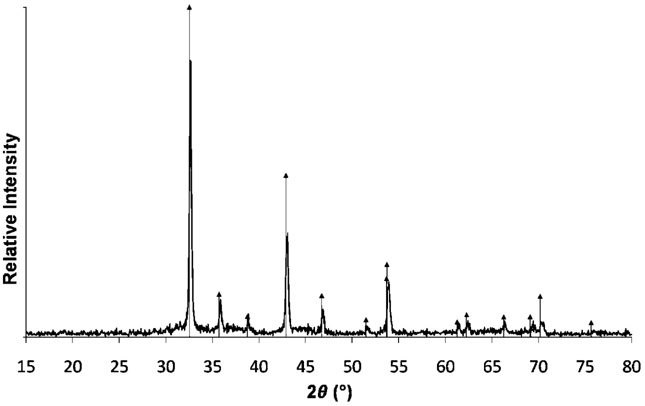

Figure 1. XRD pattern of 11 wt % K_2CO_3-promoted hydrotalcite-based material pretreated under hydrothermal conditions at 350 °C. XRD analysis was carried out in air at RT and shows the diffraction pattern of magnesite $MgCO_3$ (JCPDS 8-479; ▲). The X-ray beam wavelength corresponded to $Cu_{K\alpha}$ radiation (1.54 Å).

cesses of dehydroxylation and decarbonation that lead to the Mg(Al)O periclase crystalline phase. Thermogravimetric analysis was carried out on the resulting sample with a magnesium carbonate crystalline phase to get quantitative information about the degree of carbonation reached during treatment in the autoclave (Figure 2).

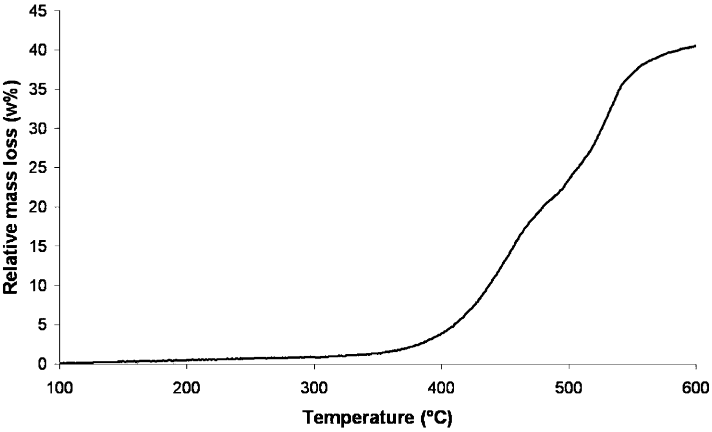

Figure 2. Thermogravimetric analysis of 11 wt% K_2CO_3-promoted hydrotalcite-based material pretreated under hydrothermal conditions at 350 °C.

The absence of any mass loss at temperatures between 100 and 350 °C is quite remarkable and confirms that the sample treated with high partial pressures of CO_2 and steam at 350 °C has undergone a radical transformation. Usually, though both unpromoted and potassium-promoted hydrotalcite-based materials have the ability to reform after decomposition at 350 °C under atmospheric pressure if allowed to cool in air in the presence of humidity,[22,27] it seems that magnesium carbonate formation by carbonation of potassium-promoted hydrotalcite-based materials prevents any rearrangement and reformation of layered double hydroxide type material if the sample is cooled in air. Previously, the presence of CO_2 in the gas phase was considered to inhibit hydrotalcite reformation after cooling of the standard decomposition product (i.e., potassium carbonate-promoted Mg(Al)O periclase phase) to room temperature. It was suggested that the presence of specific carbonates is responsible for this effect.[27] Furthermore, the mass loss between 350 and 600 °C reached a value of 41.0 wt%, which corresponds closely to the theoretical value (42.9 wt%) assuming that fully carbonated 11 wt% K_2CO_3-promoted hydrotalcite (Mg/Al 2.9) contains $MgCO_3$ instead of MgO as a result of the carbonation reaction (calculation based on a model material containing 6.6 wt% K_2CO_3 and 95.4 wt% $Mg_{2.9}(CO_3)_{2.9}AlO_{1.5}$ to give a model material with 11 wt% K_2CO_3 and 89 wt% $Mg_{2.9}AlO_{4.4}$). The assumption has been made that steam enhances formation of magnesium carbonate by partial hydration of Mg(Al)O and does not form significant amounts of hydrated alumina or hydrated analogues of magnesium carbonate. Together with the structural characterization, the thermogravimetric analysis shows that carbonation of the hydrotalcite-based material leads indeed to extensive formation of magnesium carbonate. In this case, the corresponding CO_2 capacity of 11 wt% K_2CO_3-promoted hydrotalcite (Mg/Al = 2.9) is as high as 15.2 mmol g^{-1}. This reaction leading to the formation of $MgCO_3$ seems to take place only when the partial pressure of H_2O is sufficiently high. Similarly, a CO_2 capacity of at least 11.6 mmol g^{-1} has been reported during the final regeneration cycle of a 20 wt% K_2CO_3-promoted hydrotalcite (Mg/Al = 2.9).[13] The sample had been exposed to prolonged five-step periodic cycling; the sorption reaction step was carried out with partial pressures of CO_2 and H_2O of 3.4 and 13.4 bar, respectively. Therefore, it seems that increased potassium carbonate loading (from 11 to 20 wt%) does not lead to any significant extra CO_2 sorption capacity when the carbonation reaction is carried out in the presence of high-pressure CO_2 and steam. This is contrary to what was observed in experiments carried out at atmospheric pressure.[27] An investigation into the role of potassium carbonate promotion in sorption kinetics is ongoing at this stage.

To further correlate the drastic transformation occurring in the material during carbonation, comparative SEM analyses of freshly calcined material (Figure 3) and material treated in an autoclave under high partial pressures of CO_2 and steam (Figure 4) were carried out. In both cases, the K_2CO_3-promoted hydrotalcite-based material exhibited hollow hemispherical morphologies that resulted from the thermal treatment of 11 wt% K_2CO_3-promoted commercial hydrotalcite platelets. For freshly calcined material, small, round, platelet-like particles with a size of around 100 nm could be

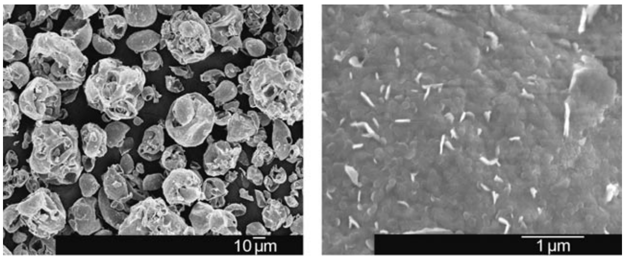

Figure 3. SEM images of 11 wt% K_2CO_3-promoted hydrotalcite-based material (Mg/Al = 2.9) freshly calcined in air at 400 °C.

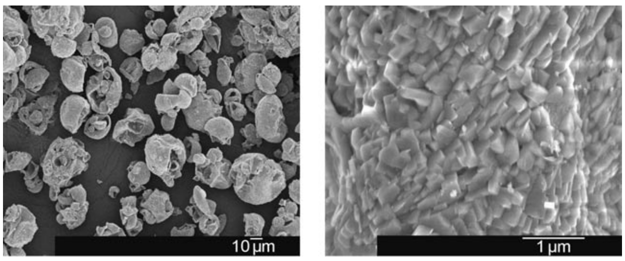

Figure 4. SEM images of 11 wt% K_2CO_3-promoted hydrotalcite-based material (Mg/Al = 2.9) pretreated in the presence of 20 bar of CO_2 and 20 bar of steam at 350 °C.

observed at the surface of large aggregates. Given their visual resemblance to the morphology of hydrotalcite platelets, these particles may have been formed while the material was exposed to ambient atmosphere between calcination and SEM analysis (several hours) according to the known reformation properties.[22] The sample treated in the autoclave (Figure 4) showed drastic morphological changes due to carbonation. The surface of the hollow hemispherical agglomerates were found to be very rough and mainly consist of rhombohedric crystallites with a size of a few hundreds of nanometres, densely packed at the surface of large aggregates. Magnesium carbonate formation clearly modifies the overall morphology of the hydrotalcite-based material on the nanometric scale. This comparative morphological study gives further evidence for extensive carbonation of the material under high partial pressures of steam and carbon dioxide. To further understand the extensive formation of magnesium carbonate in K_2CO_3-promoted hydrotalcite-based material, in situ powder XRD measurements at high partial pressures of CO_2 and steam were performed. By observing the structural rearrangement of hydrotalcite-based material in situ, it is possible to gain more detailed insight into the chemical processes occurring in the sorbent, understand the nature of the processes that trigger magnesium carbonate formation and analyse their reversibility.

A sample of 20 wt% K_2CO_3-promoted hydrotalcite (Mg/Al ratio 2.9) was calcined at 400 °C under static conditions in air, cooled in ambient conditions and then mounted into a quartz capillary for in situ XRD analysis under a total absolute pressure of up to 10 bar. Thermal decomposition of the sample up to 200 °C under 10 bar of dry CO_2 gave a typical pattern for a collapsed hydrotalcite structure ($d(003) = 6.54$ Å) together with a small amount of crystalline magnesium carbonate ($2\theta = 13.68°$, the X-ray beam wavelength was set to 0.5 Å). The crystalline hydrotalcite structure indeed lost its interlayer water molecules between 100 and 200 °C with formation of a collapsed structure in which the basal spacing distance between the hydroxide layers was significantly decreased compared with freshly precipitated hydrotalcite.[19,21,25] Furthermore, detection of a small amount of crystalline magnesium carbonate at 200 °C under these CO_2 pressures was most probably related to the thermal history of the sample. The fresh sample actually consisted of partially reconstructed hydrotalcite together with remaining periclase (Mg(Al)O) that could have indeed formed magnesium carbonate in the presence of a relatively high pressure of CO_2.[28–30]

Interestingly, when steam was added to CO_2 in a ratio of 1:1 (keeping the total pressure at 10 bar and the temperature at 200 °C), the diffraction patterns clearly indicated crystallization of several compounds coexisting with the collapsed layered double hydroxide structure. In addition to crystalline potassium carbonate, the formation of a K-dawsonite [$KAlCO_3(OH)_2$]-type phase is of particular interest. In this phase, aluminium hydroxide centres interact with potassium ions strongly enough to form new bonds. This remarkable reactivity of aluminium hydroxide centres could be related to their partial geometrical rearrangement from octahedral to tetrahedral configuration, which has been evidenced by solid-state NMR,[29] XANES[31,32] and EXAFS[33,34] measurements. It seems that the presence of relatively high partial pressures of steam and CO_2 makes tetrahedral aluminium hydroxide centres reactive enough to form mixed carbonate compounds with neighbouring potassium carbonate and/or potassium ions.[35]

Further increase of the temperature changes the situation radically: between 300 and 400 °C significant structural rearrangements take place. First, the crystalline phase corresponding to the collapsed double-layered hydroxide structure completely disappeared, in agreement with previous data on thermal decomposition of hydrotalcite. Diffraction peaks corresponding to crystalline potassium carbonate still remained visible at 400 °C, whereas other carbonate crystalline phases, such as K-dawsonite, clearly decomposed as expected from their thermal stability characteristics.[36–38] In comparison with Figure 1, diffraction peaks corresponding to crystalline potassium carbonate were more visible in this experiment, probably as a result of a higher concentration of potassium carbonate in the sample (in this experiment the sample was promoted by 20 wt% K_2CO_3, whereas a sample containing 11 wt% K_2CO_3 was used for carbonation experiment in the autoclave). Furthermore, in full agreement with the experimental data obtained from the ex situ XRD experiment (Figure 1), crystalline magnesium carbonate was the main phase observed at 400 °C. Most probably it was formed by carbonation of magnesium (hydr)oxide centres. Although it was not possible to quantify the extent of carbonation in this experiment, such direct in situ evidence of a significant formation of crystalline magnesium carbonate phase from a hydrotalcite-based material has never been reported before to the best of our knowledge. Note that the CO_2 and steam pressures used in the microcapillary reactor were lower than in the autoclave experiment and, therefore, conversion of magnesium oxide centres to magnesium carbonate might be only partial. Under atmospheric pressure, the crystalline layered double hydroxide crystalline phase usually decomposes around 350 °C to give a magnesium oxide periclase-type phase.[27,34,39] Although a magnesium oxide phase was observed during XRD experiments in the presence of 1 bar CO_2,[17] our data clearly show that the presence of high partial pressures of CO_2 and steam hinders the formation of the Mg(Al)O periclase phase and favours the formation of $MgCO_3$. It is indeed known that partial hydroxylation of magnesium oxides, such as $Mg(OH)_2$, facilitates the reaction leading to carbonate formation.[36,37]

To obtain further evidence for competition between carbonation and dehydroxylation mechanisms, an experiment simulating a pressure-swing cycle was performed (Figure 6). While the temperature was maintained at 400 °C, the gas mixture was switched from CO_2/steam (1:1) at 10 bar to pure dry N_2 and the total pressure was decreased to 1 bar. As a consequence, the 20 wt% K_2CO_3-promoted hydrotalcite-based material showed complete disappearance of $MgCO_3$ phase and the appearance of relatively sharp diffraction peaks corresponding to MgO periclase phase. The diffraction peaks of MgO observed in this experiment were much narrower than those usually measured during thermal decomposition of hydrotalcite.[27] This may be a direct consequence of precedential magnesium carbonate formation and decomposition that could have led to formation of MgO periclase structure mostly free of aluminium defects, as opposed to the periclase-like structure directly derived from hydrotalcite thermal decomposition, in which aluminium centres are still present in the distorted cubic structure. The formation of magnesia (MgO) can be actually expected considering the thermodynamics of the equilibrium between magnesium carbonate, magnesium hydroxide, magnesium oxide, steam and CO_2. At 400 °C under dry conditions in the presence of an inert gas, thermodynamic analysis has indeed shown that magnesium oxide should be the major product.[40] In addition, structural analysis showed a poorly crystalline γ-alumina-type phase that may result from phase segregation between Mg and Al that has been enhanced by the carbonation–decarbonation process. The next steps of the experiment were switching the gas mixture from N_2 to CO_2 (dry) and increasing the total pressure to 6 bar and then to 10 bar. The XRD pattern recorded at 6 bar of dry CO_2 showed no major structural changes in the material. When the pressure of dry CO_2 reached 10 bar, steam was introduced into the reactor so that the CO_2/steam ratio became 1:1 at a total pressure of 10 bar. Diffractograms in Figure 6c, d and e show the evolution of the material structure as a function of time after introduction of steam. As soon as the steam was introduced into the reactor potassium carbonate phase appeared, as was already shown in the previous experiment (Figure 5). Moreover, in the presence of steam, a magnesium carbonate crystalline phase progressively appeared again, whereas the magnesium oxide periclase phase gradually disappeared. These observations are again in agreement with the thermodynamic data on magnesium oxide, magnesium hydroxide and magnesium carbonate systems.[40] Relatively high steam partial pressure may induce partial hydroxylation of MgO periclase phase, in full agreement with the data reported by Bearat et al.[41] Furthermore, as described by Butt et al.,[42] CO_2 can then react with magnesium hydroxide compounds to give magnesium carbonate, which is favoured over simple dehydration leading back to magnesium oxide due to the pressure conditions (10 bar total pressure, steam/CO_2 1:1). In contrast to the experimental data reported by Butt et al. on pure bulk magnesia compounds, it seems that K_2CO_3-promoted hydrotalcite-based material studied in the present work can be converted almost quantitatively to magnesium carbonate, as was suggested by our TGA experiment. This difference may be caused by a combination of factors related to the composition and microstructure of the above-mentioned materials. Schaper et al. have indeed shown that the presence of alumina in the magnesium oxide structure enhances some of the properties of the resulting mixed oxide, such as surface area and basicity.[43] The presence of alumina and partially hydrated alumina phase, known to be a metastable phase under these of conditions temperature and pressure,[44] could assist reversible carbonation processes. It may enhance hydration of vicinal magnesium oxide nanoparticles, maintain a sufficiently small size of magnesium oxide particles and thus avoid diffusional limitations that are usually encountered in bulk magnesium oxide.[42] Furthermore, the promotion of hydrotalcite-based material by potassium carbonate may favour carbonation of MgO periclase nanoparticles by maintaining a sufficiently high concentration of carbonate species such as K–CO_3–Al in equilibrium with CO_2, which may catalyse formation of $MgCO_3$. As suggested by Ochoa-Fernandez et al. in their study on alkali metal zirconate materials, the presence of steam may induce higher alkali metal mobility within the mixed oxide that enhances carbonation reaction and reversible formation of bulk carbonates.[45] A

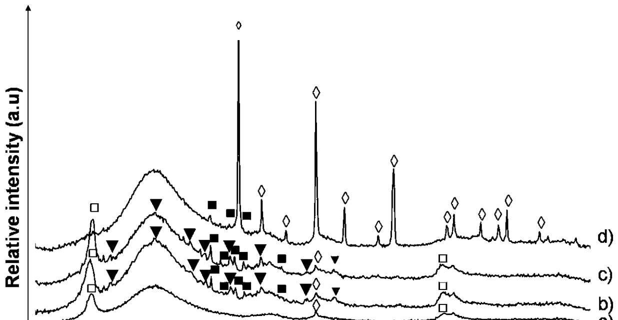

Figure 5. In situ XRD patterns of 20wt % K_2CO_3-promoted hydrotalcite (Mg/Al = 2.9) under the following conditions:. a) 200 °C, 10 bar of CO_2 (dry); b) 200 °C, 10 bar of CO_2/H_2O (1:1); c) 300 °C, 10 bar of CO_2/H_2O = 1; d) 400 °C, 10 bar of CO_2/H_2O = 1. ▼: K-dawsonite-type phase (JCPDS 21-979); □: collapsed hydrotalcite structure; ■: K_2CO_3 monoclinic phase (JCPDS 016-0820); ◇: $MgCO_3$ crystalline structure; broad background between $2\theta = 4$–10° is due to the quartz capillary. The X-ray beam wavelength was set to 0.5 Å.

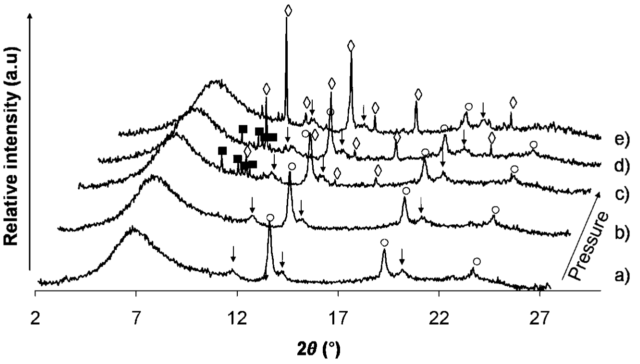

Figure 6. In situ XRD patterns of 20 wt % K_2CO_3-promoted hydrotalcite at 400 °C (Mg/Al = 2.9) under the following conditions: a) 1 bar N_2 (dry); b) 6 bar CO_2 (dry); c) 10 bar CO_2/H_2O (1:1), after 10 min; d) 10 bar CO_2/H_2O = 1, after 20 min; e) 10 bar CO_2/H_2O = 1, after 30 min. ○: MgO periclase; ■: K_2CO_3 monoclinic phase (JCPDS 016-0820); ◇: $MgCO_3$ crystalline structure; ↓: γ-alumina phase; the broad diffraction between $2\theta = 4$–10° is due to the quartz capillary. The X-ray beam wavelength was set to 0.5 Å.

contribution of both phenomena may lead to the full and reversible carbonation of MgO that can be achieved in K_2CO_3-promoted hydrotalcite-based material. Further research is ongoing to elucidate the rearrangement of alumina and potassium around magnesium oxide nanocrystallites and their role in carbon dioxide capture at relatively high partial pressures of steam.

This process of bulk carbonate formation has important repercussions for the design of gas adsorption cycles and gas adsorption units.[14–16] For instance, in a pressure-swing adsorption (PSA) design, this bulk carbonate formation (described as an absorption process) may lead to somewhat lower performance during the adsorption step by increasing CO_2 slip through the adsorption bed. Indeed this has been observed in a PSA system by using potassium-promoted hydrotalcites on the bench scale,[13] in which the slip of CO_2 in the hydrogen product gradually increased over 500 cycles. Although high CO_2 capacity may be an asset, formation of bulk carbonate by an absorption process will eventually lead to detrimentally long regeneration time or high CO_2 partial pressure in the product due to the inherent adsorption equilibrium. In contrast, the use of thermal swing adsorption could be a solution to exploit most of the available capacity under optimal conditions. The desorption temperature should be set not too high to avoid any loss of synergetic effects between potassium promotion, magnesium oxide and alumina because conversion of hydrotalcite-based material to spinel-type compounds may indeed occur at higher temperatures ($T > 500$ °C).

Conclusion

Potassium-carbonate-promoted hydrotalcite-based materials are outstanding CO_2 sorbents in the temperature range of 350 to 500 °C in the presence of relatively high partial pressures of steam and CO_2. The total CO_2 capacity of a 11 wt% K_2CO_3-promoted hydrotalcite-based material with an Mg/Al ratio of 2.9 can reach up to 15.1 $\mathrm{mmol\,g^{-1}}$ at 350 °C in the presence of sufficient concentrations of CO_2 and steam. The use of in situ structural characterization has unambiguously shown that magnesium carbonate is formed from decomposed hydrotalcite-based material under these conditions. The presence of high-pressure steam favours carbonation compared to the dehydration process leading to MgO periclase that is usually observed as result of hydrotalcite decomposition under ambient conditions and in the presence of dry CO_2. Our experiments demonstrate that it is possible to reform the magnesium carbonate phase after decomposition under a dry atmosphere by using a relatively high partial pressure of steam and CO_2, which is very interesting for industrial gas-separation processes.

Experimental Section

Hydrotalcite-based material was delivered by Sasol as commercially available Pural MG70 containing 70 wt% MgO (Mg/Al = 2.9). The as-received material was calcined at 400 °C in air and then loaded with an appropriate amount of K_2CO_3 by using an incipient wetness impregnation method. The impregnated sample was further calcined at 400 °C in air under static conditions.

Carbonation under hydrothermal conditions in an autoclave: Hydrotalcite-based material was impregnated with 11 wt% K_2CO_3 and calcined as mentioned above. Approximately 1 g of material was placed into a ceramic crucible that was suspended in a pressure bomb (Parr 4522M Pressure Reactor) consisting of a 2 L cylinder and a removable top. A measured amount of de-ionised water (21.1 mL) was added to the cylinder before the test and the ceramic sample holder was hung in the centre of the cylinder. The two parts were bolted together during operation. The sealed bomb was flushed with a CO_2 stream for about 2 min to purge air and then was pressurised to 8 bar with CO_2. An external electric heater was turned on at this point to increase the temperature in the bomb to 350 °C so that the total pressure reached about 40–45 bar. These conditions correspond to a CO_2/H_2O ratio of approximately 1:1. The system was held at this temperature and pressure for 2 h to achieve a fully loaded sample. A special procedure of removing the sample from the bomb was developed to prevent H_2O condensation on the sample and to cool it as quickly as possible. The electric heater was turned off and the pressure was released to about 15 bar. The bomb was purged with a CO_2 stream as the temperature dropped to about 150 °C. After the pressure was totally released the bomb was opened and the fully loaded sample was retrieved. The total time from turning off the heater to removing the sample from the bomb was approximately 10 min.

Thermogravimetric analysis of CO_2-loaded sample: 35 mg of the above material prepared under hydrothermal conditions was placed on the plate-like sample carrier of the microbalance of a Cahn 1100 pressurised thermogravimetric analyser (PTGA). The PTGA can operate at temperatures up to 950 °C and pressures up to 30 barg. The steam system can generate high-pressure steam up to 6 barg. A simplified schematic of the PTGA is shown in Figure 7. The reactor tube was custom-made from Inconel 600 alloy. A back-pressure regulator controlled the pressure in the unit. A high-pressure syringe pump was used to feed water into the stream. The PTGA was heated and insulated to prevent steam condensation. The TGA was flushed with 450 $\mathrm{mL\,min^{-1}}$ dry N_2, then the temperature was increased up to 600 °C at a rate of 15 $\mathrm{°C\,min^{-1}}$ and the weight changes were measured.

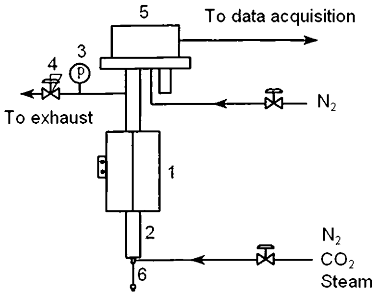

Figure 7. Simplified PTGA schematic. 1) furnace, 2) reactor tube, 3) pressure gauge, 4) back-pressure regulator, 5) balance, 6) thermocouple.

SEM characterization: SEM was performed by using an ultrahigh-vacuum JEOL scanning electron microscope (JSM-6330F). Prior to the analysis, the samples were sputter-coated with platinum.

In situ XRD with synchrotron radiation: The in situ XRD data were recorded at the SNBL (Swiss–Norwegian beam lines, BM01B) of the 6 GeV ESRF synchrotron (Grenoble, France) in a uniform-filling mode to give a typical storage-ring current of 160–200 mA. The synchrotron radiation emitted by the bending magnet (magnetic field strength: 0.4 T) was monochromatised with a channel-cut Si(111) monochromator. The X-ray beam wavelength, λ, was set to 0.5 Å. The measurements were performed by a high-resolution powder diffraction technique (two-circle diffractometer equipped with six detectors with Si(111) analyser crystals and NaI scintillation counters).

X-ray scattering measurements were performed on a narrow-sieved fraction of alkalised hydrotalcite (50–100 μm). Typically, about 10 mg of material was placed in a quartz capillary (1 mm diameter and 40 μm wall thickness, purchased from Hilgenberg, Germany), which served as microreactor. The capillary was glued to a stainless-steel sample holder with high-temperature-resistant silicon glue (Rhodorsil Silicone Elastomer, CAF-3, Rhodia) and was placed above a Cyberstar gas-blower oven supplied with N_2, which heated the sample to the desired temperature. To ensure a homogenous temperature distribution around the sample and to avoid water condensation, rigorous tracing of the gas pipes, the capillary holder and the capillary itself was achieved by using heating tapes, insulation materials and heating rods. A detailed description with picture of the cell can be found elsewhere.[35] Gas supply was controlled by a set of Bronkhorst mass flow controllers and the pressure was controlled by a back-pressure regulator (Bronkhorst). De-ionised water was pressurised by He in a stainless steel tank connected to a Bronkhorst liquid flow controller (providing the desired flow) and CEM (controlled evaporation and mixing) system heated to 200 °C. Pure gases and steam were mixed inside the CEM device in the desired quantities to obtain the desired feed gas composition and flow rate.

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