



13th International Conference on Greenhouse Gas Control Technologies, GHGT-13, 14-18
November 2016, Lausanne, Switzerland

Thermogravimetric analysis – a viable method for screening novel materials for the sorbent enhanced water-gas shift process

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Abstract

Pre-combustion CO₂ capture technologies are becoming viable alternatives to more conventional post-combustion capture by gas emissions scrubbing. The sorbent enhanced water-gas shift (SEWGS) process is a promising future technology for CO₂ capture. However, the process needs better performing materials than those available today to be competitive against state-of-the-art scrubbing technologies. Layered double hydroxides (LDH) are a promising class of materials to improve the performance of the SEWGS process. These materials have a general formula of $M^{2+}_{1-x}M^{3+}_x(OH)_2(A^{n-})_{x/n}mH_2O$, and can be tuned by substituting the metal species, changing the M^{2+}/M^{3+} ratio, adjusting the synthesis parameters to influence morphology or by adding so-called promoters to improve performance. To aid an ongoing systematic study looking at several of these parameters we have developed a simple yet efficient way of screening materials for further in-depth studies. The method is highly suitable for a typical laboratory setting, and is based on thermogravimetric analysis combined with cyclic exposure to selected gases. In this article we present the results of applying the method to a selection of benchmark materials.

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Peer-review under responsibility of the organizing committee of GHGT-13.

Keywords: CO₂ capture; SEWGS; layered double hydroxides, hydrotalcite, alkali-metal promotion, TGA, LDH

1. Introduction

The amount of anthropogenic CO₂ in the atmosphere is at an all-time high, and power production is responsible for a significant portion of the annual worldwide emissions [1]. As the world's power production from fossil fuel is likely to become more dependent on fuels with high carbon content (i.e. coal) [2], the need for more efficient CO₂ capture to reduce the impact from power production on the atmosphere is pressing. Current state-of-the-art CO₂ capture technologies include amine-based carbon scrubbing, physisorption on porous materials, intercalation in layered structures, CaO-based sorbents as well as membrane-based separation technologies [3-6]. All these technologies have in common that they separate the CO₂ from the flue gas after the fuel has been combusted. Pre-combustion CO₂ capture technologies are rapidly gaining interest as alternatives to conventional post-combustion capture. In these technologies, the carbon is separated from the fuel before combustion, resulting in a carbon free fuel (hydrogen) with CO₂-free emissions.

1.1. The sorbent enhanced water-gas shift process

The sorbent enhanced water-gas shift (SEWGS) process is a promising technology for pre-combustion CO₂ capture in power production [7]. In pre-combustion CO₂ capture processes, the fuel is reformed to give a high pressure, syngas rich (H₂ + CO) gas mixture. This gas mixture can be shifted towards higher H₂ yields through the water-gas shift (WGS) reaction by introducing steam ($\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$). *In situ* absorption of CO₂ on an appropriate sorbent shifts the equilibrium of the water-gas shift reaction significantly towards the desired product H₂, since the reaction is thermodynamically limited under standard conditions [8]. During sorbent regeneration, the carbon from the original fuel source is captured in the form of CO₂ and processed for storing. This results in a clean, decarbonized fuel for e.g. gas turbines (Figure 1).

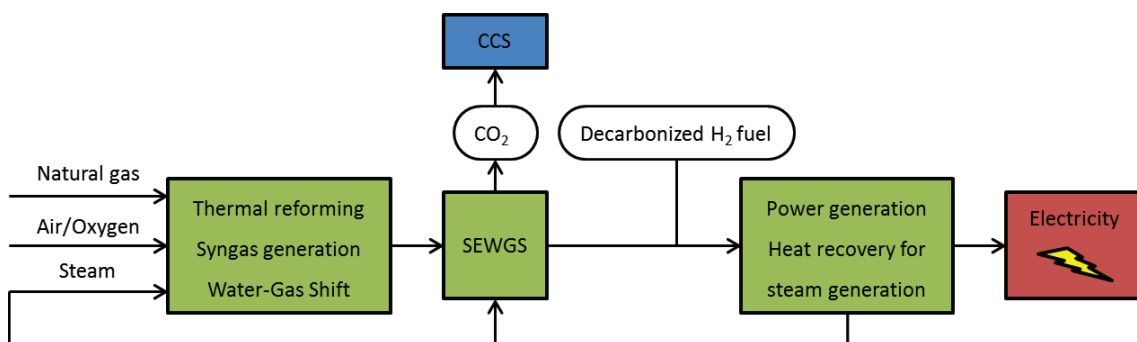


Figure 1. Schematic flow diagram of the SEWGS process.

Despite SEWGS already having reached a technology readiness level sufficient for upscaling to pilot plant scale [9], some issues remain before commercialization is feasible. Steam/energy production for sorbent regeneration is a major cost factor in carbon capture and storage (CCS). SEWGS has a low steam demand for regeneration compared to other state-of-the-art CO₂ capture technologies [9]. On the other hand, the cost for SEWGS is closely associated with the cyclic CO₂ absorption capacity of the sorbent. Hence, next generation high stability materials with good cyclic CO₂ absorption capacity will play a major role in reducing the process operating cost, making it competitive with existing amine-technologies.

The WGS reaction is slightly exothermic ($\Delta H_{298K}^0 = -41.1 \text{ kJ/mol}$) [8]. Consequently, the equilibrium is shifted towards the product side at lower temperatures. However, the kinetics of the reaction is strongly favored by higher operating temperatures. Thus, finding a material that will improve the kinetics at a lower operating temperature is of great interest to save energy in the WGS process. Alkali-metal promoted, hydrotalcite-based ($\text{Mg}_{1-x}\text{Al}_x(\text{OH})_2(\text{CO}_3)_{x/2} \cdot m\text{H}_2\text{O}$) CO₂ sorbents are promising materials for improving the SEWGS process.

1.2. The goal of the iSEWGS project

The iSEWGS project [innovative sorbents for the sorbent enhanced water-gas shift process; partners UiO (NO), SINTEF (NO), ECN (NL) and Politecnico di Milano (IT)] addresses two primary targets. One is finding materials that have good cyclic CO₂ absorption capacity under operating temperatures. The second is finding materials that reduce the necessary temperature both for absorption and desorption of CO₂. Reducing the temperature for absorption is beneficial for the equilibrium of the WGS reaction, and also reduces the energy needed for sorbent regeneration. Both effects are critical in reducing the operating costs of the SEWGS process.

Among the materials being studied in the project is a range of Mg-Al based layered double hydroxides (LDH). The structure of these materials consist of brucite-like layers [Mg(OH)₂ in edge-shared octahedra] with partial substitution of the Mg²⁺ sites with Al³⁺, inducing a positive charge in the layers [10]. This positive charge is compensated by anions located in the interlayers. Synthesis targets include LDH-materials with additional metal substitution beyond Mg and Al, as well as various degrees of alkali metal (K or Na) promotion. The effect of varying the M²⁺/M³⁺ ratio in the LDH is of great interest, in addition to investigating the effect the pH during synthesis has on the morphology of the materials. The effect of activating/calcining the LDH before alkali-metal impregnation is also explored in the iSEWGS project. Selected interesting lead samples will be subjected to in-depth analysis. This includes analysis of sorption behavior under realistic industrial conditions, as well as investigation by several other techniques such as powder X-ray diffraction (P-XRD), solid-state nuclear magnetic resonance (NMR) and infrared spectroscopy (FT-IR). In this work we evaluate the possibility of using a widely accessible technique, thermogravimetric analysis (TGA), to provide qualitative information on lead materials.

2. Materials and methods

2.1. Synthesis

The starting materials and solvents were obtained from commercial suppliers (Sigma-Aldrich and VWR), and used without additional purification. Benchmark Mg-Al-LDH materials with Mg²⁺/Al³⁺ ratios of 2:1, 3:1 and 4:1 were synthesized by co-precipitation techniques [11]. The following procedure is representative of a typical synthesis procedure. 50 mL of de-ionized water was heated and kept at 60 °C in a round bottom flask under ambient atmosphere. Meanwhile, cation and anion solutions were prepared separately from the mother liquor. A cation solution for a 3:1 Mg-Al-LDH was prepared by dissolving Mg(NO₃)₂·6H₂O (19.23 g, 75 mmol) and Al(NO₃)₃·9H₂O (9.38 g, 25 mmol) in 25 mL of de-ionized water. The anion solution was a stock solution, pre-made in batches by dissolving KOH (190.77 g, 3.40 mol) and K₂CO₃ (138.21 g, 1.00 mol) in 1 L of de-ionized water. A peristaltic pump (Watson Marlow 101U/R) was used to add the cation solution to the mother liquor at a fixed rate. A second peristaltic pump, attached to a control box (Mettler Toledo 2220) with a pH-probe (Knick SE 555X), was used to add the anionic solution. The control box regulates the addition of the anionic solution to ensure a pH in the reaction vessel of 11.0. After the cation solution had been added, the solution was stirred for 60 minutes. During this period, the control box for the anion solution ensures a steady pH, as the pH otherwise has a tendency to decrease slightly over time. After the post-stirring, the solution was left to rest without stirring for 60 minutes at 60 °C. The synthesis product was washed by centrifuging the reaction mixture, decanting off the mother liquor and resuspending the LDH in de-ionized water, typically 4 times before the final centrifugation. To obtain the finished product, the LDH was dried, either in a conventional oven or by freeze drying.

2.2. Alkali-metal promotion

Alkali-metal promotion was performed by weighing out the desired amount of dry LDH and the desired amount of alkali-metal promoter (e.g. 20 wt% K_2CO_3). In the cases where the LDH had been dried in a conventional oven, the sample was subjected to gentle grinding in a mortar. Then, the mixture of LDH and promoter was suspended in a small amount of de-ionized water and left at room temperature for 24 hours. Finally, the mixture was dried to yield the final promoted LDH.

2.3. Thermogravimetric analysis and Differential Scanning Calorimetry

Thermogravimetric analysis and differential scanning calorimetry (TGA/DSC) was performed on a Netzsch STA 449F1 TG-instrument in platinum crucibles. A gas controller fitted to the instrument enables switching between two gases during the experiment. The instrument was normally set up with gas flows of 25 and 50 mL/min for the protective (N_2) and experimental (N_2/CO_2) gas, respectively. Hence, the most common atmospheres used for the experiments consist of either 100 % N_2 or approximately 67 % CO_2 in N_2 at ambient pressure. The measurements were baseline corrected using the Proteus software package.

3. Results and discussion

In a systematic search for new materials, the number of samples generated can be daunting and selecting the most interesting lead materials can be a challenge. Additionally, subjecting all samples to full and exhaustive analysis can become prohibitively time consuming and expensive. Early on in the project it became clear that there was a need for a simple experimental setup to provide a metric for determining the most interesting lead materials for further, more thorough testing. Techniques like P-XRD or surface area measurements (e.g. BET adsorption) were considered due to the relative ease and speed of such measurements. However, LDH materials produced with co-precipitation techniques typically have very poor crystallinity when compared to samples produced with e.g. the urea method [12-14]. This creates challenges in determining minute structural differences in the samples by XRD. In addition, LDH materials tend to have strong preferred orientation which necessitates sample preparation in capillaries for XRD analysis. Compared to analysis of samples prepared on flat-plate sample holders, capillary measurements are more time consuming. Surface area measurement was also discarded as screening method, since it was unclear if it would provide the desired metric for evaluating the samples. Acknowledging that cyclic CO_2 sorption is a critical parameter in evaluating the performance of the materials, we looked at ways to simulate an industrial sorption experiment with simple laboratory instruments that are readily available. Thermogravimetric analysis under different atmospheres seemed a viable option. The hypothesis was that we could mimic an industrial sorption experiment by exposing the sample to different atmospheres at industrially relevant temperature, albeit under more idealized conditions (e.g. dry atmospheres at ambient pressure). A series of both isothermal and variable temperature cyclic sorption experiments was set up to analyze several benchmark Mg-Al-LDH materials.

3.1. Thermogravimetric analysis as a method for screening new samples

Performing combinations of variable temperature and isothermal cyclic sorption measurements provides a large amount of data. This type of analysis can be used to evaluate not only the absolute sorption capacity of the material, but also at which temperature the sorption capacity is at its maximum. Careful analysis of the data also provides some qualitative indications on at which temperature the sorption kinetics is acceptable. In addition, subjecting a material to rigorous multi-cycle sorption experiments provides information regarding the long-term stability. All these four metrics, sorption capacity, sorption temperature, multi-cycle stability and sorption kinetics are important when evaluating the performance of a new material.

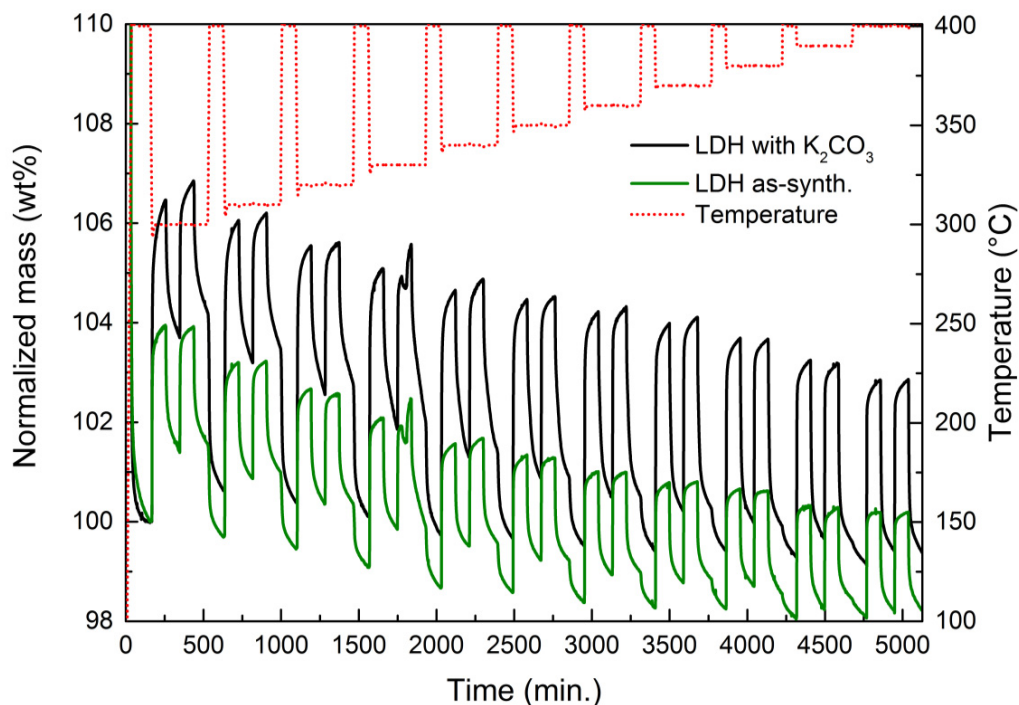


Figure 2: An example of a variable temperature sorption experiment. The mass percentages have been normalized by setting the mass of the samples after the initial activation to 100 %. The anomaly in the second absorption cycle at 330 °C (approx. at 1800 min.) is an artefact from the instrument.

Figure 2 illustrates a typical variable temperature sorption experiment. This particular experiment shows the results from CO₂ sorption on a Mg-Al-LDH with a Mg²⁺/Al³⁺ ratio of 3:1, with and without alkali-metal promotion with 20 wt% K₂CO₃. Initially, the samples were activated by heating to 400 °C for 2 hours under a pure N₂ atmosphere. The samples were then cooled to 300 °C and exposed to alternating 90 minute cycles of CO₂-rich (67 % CO₂ in N₂) and pure N₂ atmospheres. Re-activation of the samples was performed by heating them to 400 °C for 90 minutes in a pure N₂ atmosphere. This process was repeated for temperatures from 300 to 400 °C in 10 °C increments. The selection of activation temperature as well as cycle duration was based on results from the initial investigations. Activating the sample at a too high temperature had a slightly negative impact on the performance of the materials. XRD analysis indicated that the high activation temperature led to irreversible formation of a MgO rock-salt phase (not shown here), a well known issue in high temperature treatment of LDH-materials [15]. The initial cycling experiments had cycle duration of 180 minutes. However, the mass changes in the second half of the cycle were small relative to the maximum sorption. Thus the cycle time was reduced to 90 minutes to shorten the experiment time while retaining a satisfactory level of maximum sorption.

This type of experiment provides a large amount of qualitative information on the sample. From the example illustrated in Figure 2, it is obvious that the alkali-metal promotion with K₂CO₃ has a significant impact on the CO₂ sorption behavior of the material. The alkali-metal promoted material far outperforms the non-promoted equivalent (the exact same batch without promotion) with regards to sorption capacity. This is a trend we have observed over several Mg-Al-LDH materials with various Mg²⁺/Al³⁺ ratios. This trend is also consistent with literature findings [16]. Furthermore, it is clear that the first absorption cycle after activation differs significantly from subsequent sorption cycles. This feature is important to take into account when evaluating the cyclic rather than the absolute CO₂ sorption capacity of the material in question.

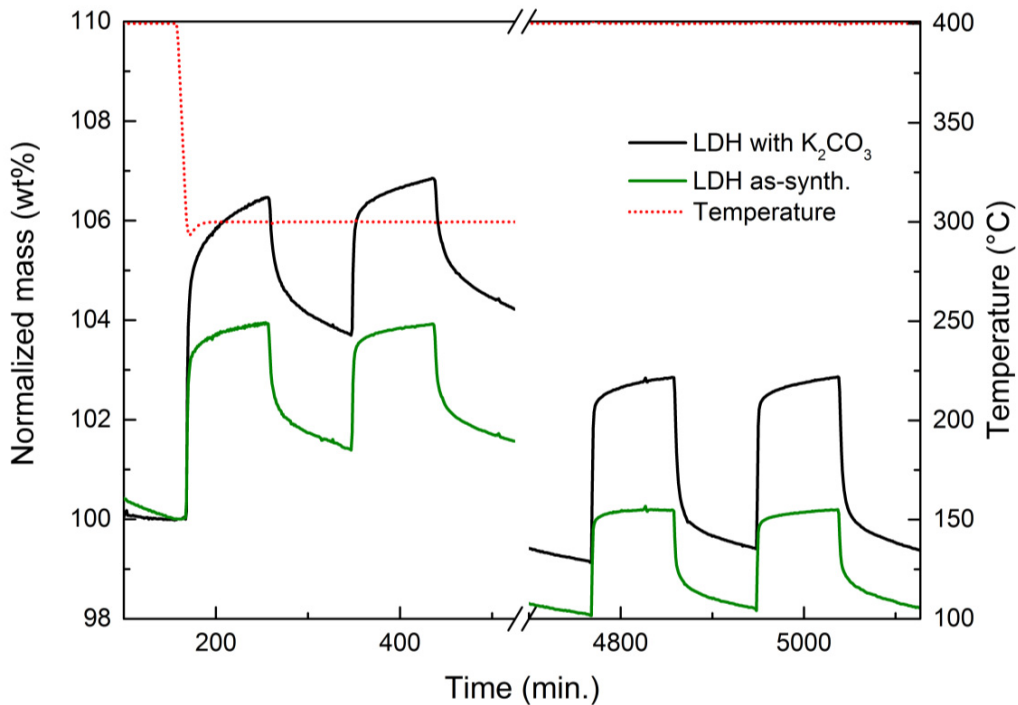


Figure 3: Excerpt from the variable temperature sorption experiment illustrated in Figure 2.

Looking more closely at the shape of the absorption curves, reveals qualitative information regarding the kinetics of the sorption process. Figure 3 shows a close-up of the sorption curves recorded at 300 and 400 °C. The sorption curves at 300 °C have a more rounded shape than the curves at 400 °C, especially in the desorption curve. This suggests that the material requires more time for its absorption capacity to reach saturation at the lower temperature. Additional information could be gathered by calculating the 1st derivative of the sorption curve. This shows where the absorption is approaching its maximum, by seeing where the rate of change intercepts a preset value as it approaches zero. By doing so, it became clear that desorption is a slower process than absorption at lower temperatures (see discussion below).

The sorption results can be further manipulated to extract even more data, this time regarding the optimal temperature for the sorption process from a capacity point of view. Figure 4 details the CO₂ sorption behavior of three Mg-Al-LDH materials with different Mg²⁺/Al³⁺ ratios (2:1, 3:1 and 4:1), with and without alkali-metal promotion, plotted as a function of temperature. The absorption values have been extracted by subtracting the lowest absolute value of the preceding desorption step from the maximum absolute value from the absorption step (see equation 1), and *vice versa* for the desorption values. Note that the values of the first absorption cycle are, generally speaking, not representative of the consecutive cycles, and have been left out to avoid distorting the results (see Figure 2). To smooth out any outliers and ensure a more realistic image of cyclic capacity, the values presented in the plots are the averages from the two sorption cycles recorded during the experiments at each temperature.

$$wt\%_i^{abs} = wt\%_i^{max} - wt\%_{i-1}^{min} \quad (1)$$

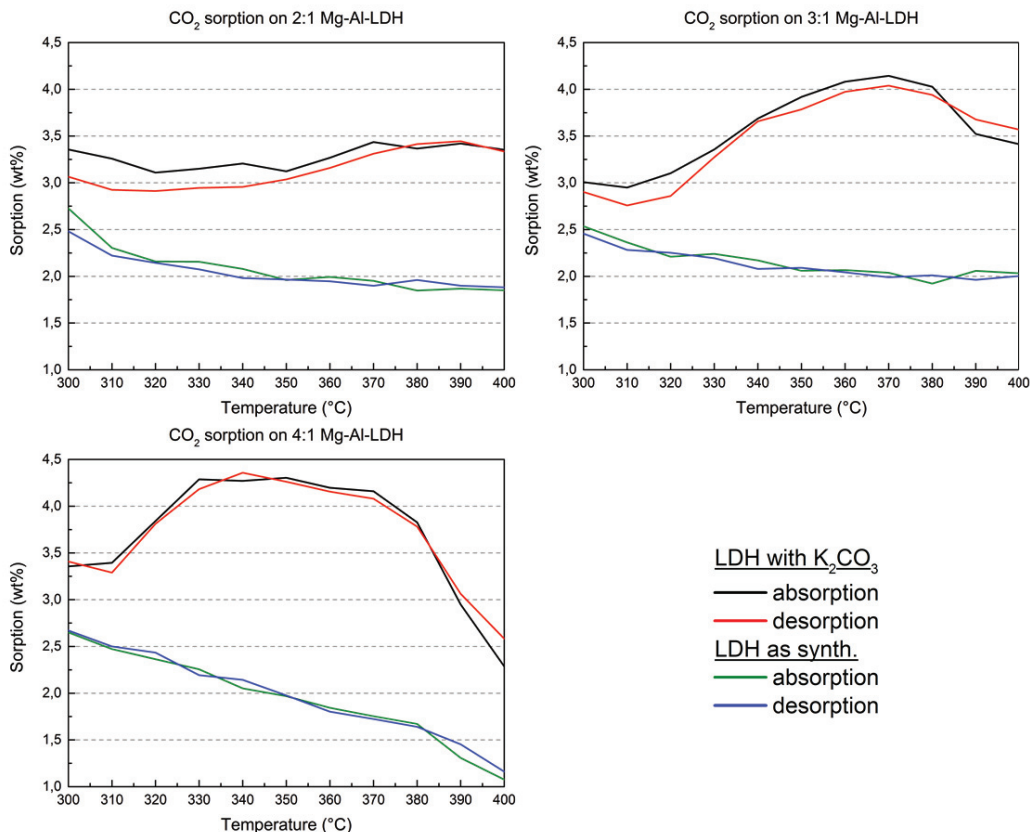


Figure 4: Curves showing the average sorption of CO₂, plotted against temperature, in three different Mg-Al-LDH materials with and without alkali-metal promotion. 2 wt% sorption \approx 0.454 mmol CO₂/g sorbent.

By comparing the graphs in Figure 4, we can see some significant differences in the behavior of the three materials. First of all, the obvious capacity differences observed in Figure 2 between the promoted and as-synthesized samples become very clear. In the case of the 3:1 Mg-Al-LDH in Figure 4, the cyclic CO₂ sorption capacity is in fact doubled by the promotion at 370 °C. We can also see that the as-synthesized samples have quite comparable sorption capacities over the range of Mg²⁺/Al³⁺ ratios. Secondly, it is clear that the alkali-metal promotion has a big impact on the thermal response of the materials. In the as-synthesized samples, it seems that increasing the temperature in the sorption process has a slightly negative impact on the capacity. In contrast, the promoted samples generally show an increase in cyclic CO₂ sorption capacity with temperature, up to about 370 °C where the capacity starts to decrease. Temperatures above 380 °C seem to have a particularly detrimental effect on the performance of the 4:1 Mg-Al-LDH. It is worth pointing out that the three different samples presented here all reach their maximum sorption at different temperatures. As mentioned earlier, a lower temperature favors product formation in the WGS reaction. Thus a material with a slightly lower absolute cyclic sorption performance, but which performs well at a lower temperature can be the better option for the SEWGS process as a whole.

Isothermal cyclic sorption experiments can be used to compliment and support the information gathered in variable temperature experiments. In particular, they can reveal the stability of the performance of the material over time. Figure 5 details a typical isothermal cyclic sorption experiment, performed on a 3:1 Mg-Al-LDH promoted with 20 wt% K_2CO_3 . Like in the previously described variable temperature experiment, the material was activated by heating it to 400 °C for 2 hours under a pure N_2 atmosphere. The sample was then cooled to the temperature selected for closer investigation (350 °C) and exposed to alternating 90 minute cycles of CO_2 -rich (67 % CO_2 in N_2) and pure N_2 atmospheres. From Figure 5 (left), we can see that the initial cycles differ somewhat from subsequent cycles. This could be interpreted as the cycle duration of 90 minutes being slightly too short to fully saturate the material in the first two cycles. However, the sorption can be plotted as maximum sorption per cycle similarly to Figure 4. Regardless of the slightly differing behavior in the initial cycles, we can see from Figure 5 (right) that the performance is in fact relatively stable over the 12 cycle experiment. The sorption holds at around 3.5 to 4.0 wt% or about 0.8 to 0.9 mmol CO_2/g sorbent over the course of the experiment. This performance is in agreement with the data collected through the variable temperature sorption experiments displayed in Figure 4.

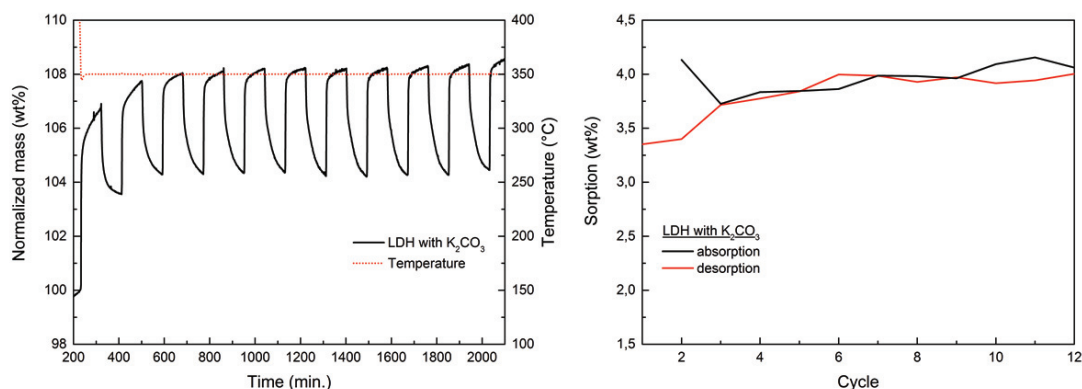


Figure 5: (left) An example of a isothermal sorption experiment. The mass percentages have been normalized by setting the mass of the samples after the initial activation to 100 %. (right) Curves showing the sorption of CO_2 , plotted against sorption cycle in the isothermal experiment. The first absorption cycle has been omitted. 2 wt% sorption \approx 0.454 mmol CO_2/g sorbent.

Figure 6 shows an example of how qualitative sorption speed data could be extracted from a cyclic sorption experiment by calculating the 1st derivative of the mass. The dataset was collected on a 3:1 Mg-Al-LDH promoted with 20 wt% K_2CO_3 , the same dataset as displayed in Figure 3. In the figure, the normalized mass is shown with a black line, and the 1st derivative of the mass in red. Visual aides are added as grey dashed lines at $y = \pm 0.0075$. Green and blue bars indicate the time duration between the switch to and from the CO_2 -rich atmosphere, and to the point where the rate of sorption has decreased below the selected value of ± 0.0075 . Open ended bars signify that the sorption does not reach the selected level within the 90 minutes of the sorption cycle. The intercept values of ± 0.0075 were selected as indication of where the sorption is reaching a flat plateau, or in essence where the material is approaching its saturation level.

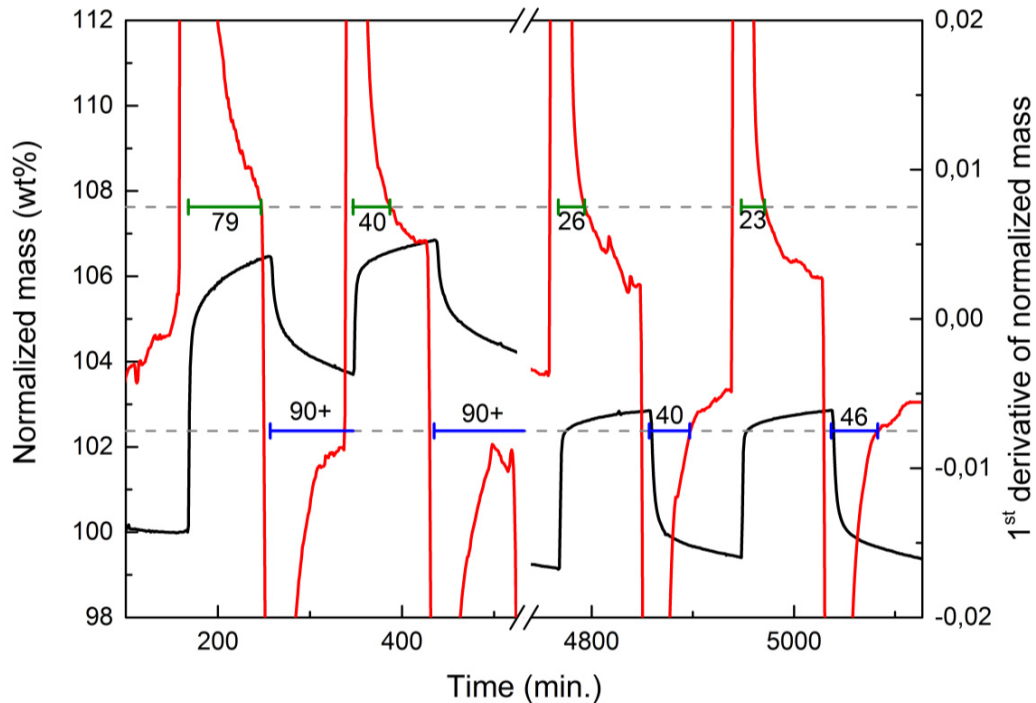


Figure 6: Example of qualitative sorption speed data extraction from a cyclic sorption experiment by calculating the 1st derivative of the mass.

Figure 6 shows clear trends with regards to differences in absorption and desorption, as well as differences in sorption at high and low temperatures. At 300 °C (100 to 525 minutes), we can see that the absorption rate reaches the pre-determined level markedly faster than the desorption rate. In fact, the desorption curve does not intercept the dashed line at $y = -0.0075$ within the 90 minutes of the sorption cycle. As a consequence, the absorbed CO₂ gas will accumulate over time and the performance will likely decrease in an experiment with additional sorption cycles (e.g. an isothermal sorption experiment), unless the cycle duration is changed. The sorption time of the first absorption cycle (79 minutes) should also be commented on. The first cycle takes significantly longer than the second cycle (40 minutes), and it could also be argued that the intercept with $y = 0.0075$ coincides with the change to a pure N₂ atmosphere (desorption) distorting the result slightly. Over the course of several experiments, we have seen indications pointing towards slower kinetics in the first absorption cycle after initial activation. This should be taken into account in future design of sorption experiments. By comparison, the sorption times at 400 °C (4740 to 5127 minutes) are much shorter than the ones observed at 300 °C. We can see absorption and desorption times of around 25 and 43 minutes, respectively. Similarly to the sorption times observed at 300 °C, there is a clear trend that absorption is a faster process than desorption. However, at 400 °C the cycle time seems more than sufficient to ensure satisfactory absorption and desorption. Hence there is little to suggest that CO₂ is accumulating in the material at these temperatures with the selected cycle duration.

4. Conclusions

In this article we have investigated the viability of using thermogravimetric analysis, a commonly available technique, for screening new sorbent materials for the SEWGS process. The method is based on both variable temperature and isothermal cyclic sorption experiments where the sample is exposed to different atmospheres. We have demonstrated that in this way, a large amount of qualitative sorption data can be collected in an efficient, highly automatable manner. We have collected sorption data series on a selection of Mg-Al-LDH materials, and the trends in the results are consistent with literature findings. Thus the method seems to fulfil the intended role of providing a simple metric for selecting interesting samples for in-depth analysis. Future work will involve rigorous testing of selected samples under realistic industrial conditions to compare the results from the current study. Depending on the consistency between the screening and the extensive sorption testing, the method will be used in a systematic study of new sorbent materials for the SEWGS process.

Acknowledgements

We acknowledge the support from the Research Council of Norway (project #243736), and the use of the Norwegian national infrastructure for X-ray diffraction and scattering (RECX) at UiO.

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