DEVELOPMENT OF SYNTHETIC, Ca-BASED SORBENTS FOR CO_2 CAPTURE USING THE CO-PRECIPITATION TECHNIQUE

**M. Broda, A. M. Kierzkowska and C. R. Müller**

muelchri@ethz.ch

Institute of Energy Technology, Department of Mechanical and Process Engineering, ETH Zurich,
Leonhardstrasse 27, 8092 Zurich, Switzerland.

Abstract

Co-precipitation was employed to synthesize Ca-based, Al_2O_3-stabilized sorbents for CO_2 capture. The chemical composition and morphology of the synthesized sorbents were characterized using scanning electron microscopy, X-ray diffraction and N_2 adsorption analysis. The cyclic CO_2 uptake of the synthetic sorbent was studied in a thermo-gravimetric analyzer and compared to limestone. It was found that the calcium precursor, precipitation agent as well as the pH value at which the precipitation was performed, strongly influenced the chemical composition and morphology of the precipitated sorbents and, in turn, their cyclic CO_2 uptake capabilities. Sorbents which were synthesized using $Ca(NO_3)_2$ as the calcium precursor, and precipitated with Na_2CO_3 at pH 7.0 showed the best cyclic CO_2 uptake capability. The CO_2 capture capacity of the best synthetic sorbent was 0.32 g CO_2/g sorbent after 30 cycles of calcination and carbonation, which compares favourably to the CO_2 uptake of limestone of 0.20 g CO_2/g sorbent. Correlating the volumes in pores with pore radii narrower than 100 nn with the CO_2 uptake capacity of the synthetic sorbents indicated that sorbents which possess a high pore volume equally show high CO_2 uptake capabilities.

Introduction

The emission of anthropogenic CO_2 from the combustion of fossil fuels has led to an increase in the concentration of CO_2 in the atmosphere from a pre-industrial level of ~ 280 ppm to its current level of ~380 ppm [1]. This significant increase in CO_2 concentration is almost certainly linked to long-term climate change. Coal is the world's most important source of electricity accounting for ~ 40 % of worldwide production [1]. Despite coal being one of the most polluting fossil fuels in terms of mass of CO_2 emitted per unit of power generated, its use is projected to more than double by 2030 [1]. It is, therefore, imperative to find ways of using coal which limit the release of CO_2 into the atmosphere. Current CO_2 separation technology relies on scrubbing the flue gases with, *e.g.* monoethanolamine (MEA), as it has been demonstrated on the industrial scale for *e.g.* natural gas purification. However, MEA scrubbing comes with a large energy penalty because of the large heat requirement for regeneration [2]. Furthermore, amine-based solvents are sensitive to typical flue gas impurities, such as SO_x and NO_x, and therefore require expensive gas clean-up technology. Because of these shortcomings, significant research is currently being performed in both academia and industry to develop less costly CO_2 capture techniques. One of these emerging CO_2 capture technologies is the use of calcium-based sorbents that undergo calcination and carbonation reactions, *viz.*

$$CaO(s) + CO_2(g) \leftrightarrow CaCO_3(s) \quad (1)$$
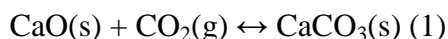
Due to the high operating temperature of the carbonation ($T \sim 600 - 700$ °C) and calcination ($T > 900$°C) reactions, the calcium looping cycle potentially has a significantly smaller energy penalty than amine scrubbing [3]. A further advantage of calcium-based CO_2 sorbents compared to other solid sorbents, such as hydrotalcites, zeolites or lithium zirconate, is the high theoretical capture capacity of 0.78 g CO_2/g CaO. The overwhelming majority of research in the field of calcium-based CO_2 sorbents has focused on natural sorbents, such as limestone and dolomite. However, CaO derived from natural sorbents rapidly losses its capacity to react with CO_2 after repeated cycles of calcination and carbonation [4,5]. Abanades and Alvarez [6] reviewed the decay of carrying capacity with cycle number for various limestones and experimental conditions. They showed that the decay of carrying capacity with number of cycles correlates only weakly with the experimental conditions and were able to summarize various measurements by an empirical correlation, correlating the carrying capacity with cycle number. Similar correlations have been proposed by other groups, *e.g.* [7]. Experiments performed over 1000 cycles have supported the argument that limestone has an asymptotic conversion of about 7 % [8]. So far, the question of what causes this rapid loss of cyclic CO_2 capture capacity in natural sorbents has not been answered unequivocally. However, based on SEM images, Brunauer-Emmett-Teller (BET) surface area and Barret-Joyner-Halender (BJH) pore size distribution measurements, sintering in the micro-granular network in the calcine, the filling and blockage of small pores, and the formation of a layer of product on the outer walls of the grains have been proposed as possible explanations for the loss of CO_2 capture capacity [8-10]. Owing to the shortcoming of natural sorbents, there is an urgent need to develop synthetic sorbents which possess a high carrying capacity of CO_2 over repeated calcination-carbonation cycles. One approach to synthesize such stable sorbents has been to stabilize CaO with an inert compound. For example, Li *et al.* [11] used a hydrolysis technique to mix CaO with mayenite ($Ca_{12}Al_{14}O_{33}$). Particles with $d_p = 45$ μm where tested in a TGA and stable conversions were reported over 13 cycles; The carrying capacity of the synthetic sorbent after 13 cycles was ~ 0.4 g CO_2/g sorbent compared to ~ 0.3 g CO_2 / g sorbent for a dolomite. The hydrolysis technique of Li et al. [11] was extended by Pacciani *et al.* [10,12], who observed that the initially low reactivity of their synthetic sorbents increased in subsequent cycles and surpassed the performance of limestone after 20 cycles. Additionally, mechanical mixing techniques have been applied to stabilize CaO with inert supports. For example, Wu *et al.* [13] mixed nano- and micro-sized $CaCO_3$ with Al_2O_3, bentonite and kaoline. $CaCO_3$ supported with Al_2O_3 showed the best cyclic stability, which was attributed to the formation of mayenite. However, owing to the comparatively small amount of CaO in the mixture (35 wt.%), the CO_2 capture capacity was only ~ 0.15 g CO_2/g sorbents after 50 cycles, which is not very different from limestone. A shortcoming of the majority of the current approaches to synthesize sorbents is the application of rather simple synthesizing techniques, *e.g.* wet impregnation or mechanical mixing, which do not allow key structural properties of the sorbent, such as pore size distribution, to be tailored easily. In this work, we use the co-precipiation technique to synthesize calcium-based CO_2 sorbents, which show very favourable CO_2 capture characteristics compared to limestone.

Experimental

First, an aqueous solution containing 0.8 M of $Ca(NO_3)_2$ (or $Ca(C_2H_3O_2)_2$) and 0.2 M of $Al(NO_3)_3$ was prepared. The corresponding mass ratio of CaO to Al_2O_3 was 81:19. A 1.0 M solution of Na_2CO_3 was subsequently added slowly to the stirred (350 rpm) solution to precipitate out $CaCO_3$ and $Al(OH)_3$. During addition of Na_2CO_3 the pH value of the solution was monitored with a pH meter. The amount of Na_2CO_3 added was determined by the desired final pH values of 7.0 and 9.7. Subsequently, the precipitates were aged for 2 h and washed to

remove Na^+ cations. Washing was stopped once the conductivity of the decanted water was below 100 μS/cm. The washed precipitates were subsequently vacuum-filtered, dried in an oven at 100 °C overnight, followed by calcination in air in a muffle furnace at 800 °C for 2 h. To investigate the influence of the precipitation agent, solutions containing 0.8 M of $Ca(NO_3)_2$ and 0.2 M of $Al(NO_3)_3$ were precipitated using a 35 vol. % aqueous solution of NH_3. Precipitation was performed at pH 7.0 and 9.7.

The surface area, pore volume and pore size distribution of the synthetic sorbents were determined using a Quantachrome NOVA 4000e analyzer. Prior to the N_2 adsorption analysis, each sample was degassed at 300 °C for approximately 3h. The Brunauer *et al.* [14] (BET) model and the Barrett *et al.* [15] (BJH) model were used to calculate the surface area and the pore size distribution of the sorbents, respectively

A scanning electron microscope (FEI Quanta 200 FEG) was used to characterize the morphology of the precipitated sorbents. A double-sided carbon tape was used to attach samples of the sorbent onto a 12.5×10 mm aluminium holder. Prior to imaging, the samples were sputter coated with gold (SCD 050).

The crystallinity and chemical composition of the synthesized sorbents were evaluated using X-ray powder diffraction (Bruker, AXS D8 Advance, equipped with a Lynxeye superspeed detector operated at 40 mA and 40 kV). Each sample was scanned in the 2θ range of 5-90°. The step size was 0.025° and the scan time per step was 0.8 s.

The cyclic CO_2 capture capacity of the synthetic Ca-based sorbents was evaluated using a thermo-gravimetric analyzer (TGA, Mettler Toledo TGA/ DSC 1). A small amount (< 50 mg) of calcined sorbent was placed in a 70 μl alumina pan and heated up to the carbonation temperature of 750 °C at a rate of 10 °C/min under a flow of 20 cm^3/min N_2. Additionally, a constant flow of N_2 of 25 cm^3/min was used as a purge flow over the micro-balance. Once the carbonation temperature was reached, a CO_2 flow of 30 cm^3/min was introduced into the TGA. Thus, carbonation was performed in an atmosphere containing 40 vol. % CO_2 and 60 vol. % N_2. After 20 mins. of carbonation, the CO_2 flow was stopped for 20 min to allow the calcination reaction to proceed. The carbonation/calcination cycle was repeated up to 30 times for each sorbent. The cyclic CO_2 uptake of sorbents [g CO_2/g sorbent] and the conversion of CaO present in the sorbent (assuming that all Ca was precipitated out), were calculated from the continuously recorded weight changes during calcination and carbonation.
.

Results

The cyclic CO_2 uptake, determined as g CO_2/g sorbent and conversion of CaO present in the sorbent are plotted in Fig. 1. As a benchmark the cyclic CO_2 uptake and CaO conversion of a natural sorbent, Havelock limestone, is also plotted in Fig. 1. For Havelock limestone, a very high CO_2 uptake of 0.54 g CO_2/g sorbent, corresponding to a CaO conversion of 0.69 of the CaO in the limestone, was observed for the first cycle. However, with cycle number the CO_2 uptake decreases rapidly. After 10 cycles the CO_2 uptakes was 0.30 g CO_2/g sorbent, corresponding to a CaO conversion of only 0.38. Thus, the average decay rate of the CO_2 uptake with cycle number is 4.4 % per cycle as determined from the 10 cycles experiment. The observations made here for Havelock limestone are in good agreement with previous studies for different limestones [4,16]. Figures 1(b) and (d) show the CO_2 uptake of the synthetic sorbents precipitated at pH 7.0 and 9.7, respectively. From Figs. 1(b) and (d) it is clear that precipitation with NH_3 resulted in a material which did not react with CO_2, regardless of the pH value at which the precipitation was performed. On the other hand, co-precipitation of a solution of $Ca(C_2H_3O_2)_2$ and $Al(NO_3)_3$ with Na_2CO_3 yielded sorbents with good, cyclic CO_2 uptake. The CO_2 uptake during the first cycle for sorbents precipitated at pH 7.0 and 9.7 were, respectively, 0.42 and 0.49 g CO_2/g sorbent, which corresponds to CaO conversions of 0.6 and 0.76. After the 10th cycle the CO_2 uptakes had decreased to 0.29 and

0.35 g CO_2/g sorbent, which corresponds to CaO conversions of 0.46 and 0.54, respectively. Thus, the average rates of decay of the CO_2 uptake with cycle number were 3.1 % and 3.3 % per cycle, respectively. Comparing the CO_2 uptake of the sorbents precipitated using $Ca(C_2H_3O_2)_2$ as the calcium precursors with limestone, shows that the sorbents synthesized at pH 7.0 and 9.7 possess slightly lower and higher CO_2 uptakes, respectively. With respect to
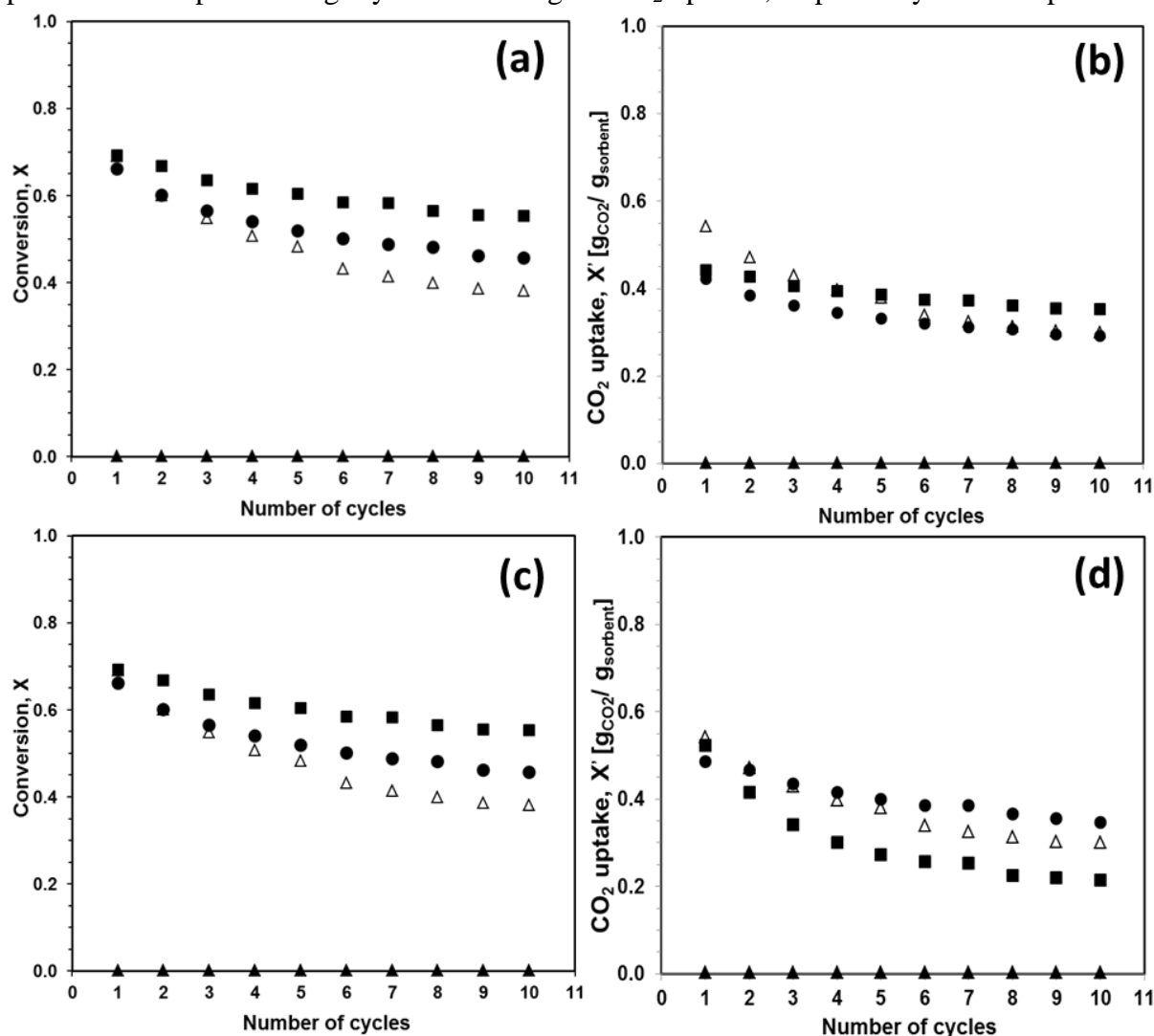

Figure 1. Cyclic CaO conversion and CO_2 uptake for synthetic and natural sorbents obtained from TGA measurements. The carbonation and calcination temperature was 750 °C: (•) $Ca(C_2H_3O_2)_2$ and Na_2CO_3, (■) $Ca(NO_3)_2$ and Na_2CO_3, (▲) $Ca(NO_3)_2$ and NH_3 and (△) Havelock limestone: (a,b) pH = 7.0, (c,d) pH = 9.7.

the decay rate, the sorbents synthesized using $Ca(C_2H_3O_2)_2$ as the calcium precursors significantly outperformed limestone.

Figures 1(b) and (d) show that the best synthetic sorbent with respect to high and stable CO_2 uptake, is obtained when $Ca(NO_3)_2$ and $Al(NO_3)_3$ are precipitated at pH 7.0 with Na_2CO_3. Using $Ca(NO_3)_2$ as the calcium precursor, the CO_2 uptakes for the first cycle were 0.44 and 0.52 g CO_2/g sorbent, which corresponds to CaO conversions of 0.69 and 0.82, for precipitation performed at pH 7.0 and 9.7, respectively. After the 10th cycle the CO_2 uptakes had decreased to, respectively, 0.35 and 0.21 g CO_2/g sorbent, corresponding to CaO conversions of 0.55 and 0.33. Thus, the average rates of decay of the CO_2 uptake with cycle number were 2.0 % and 6.0 %, respectively. From Fig. 1(b) it can be seen that starting from
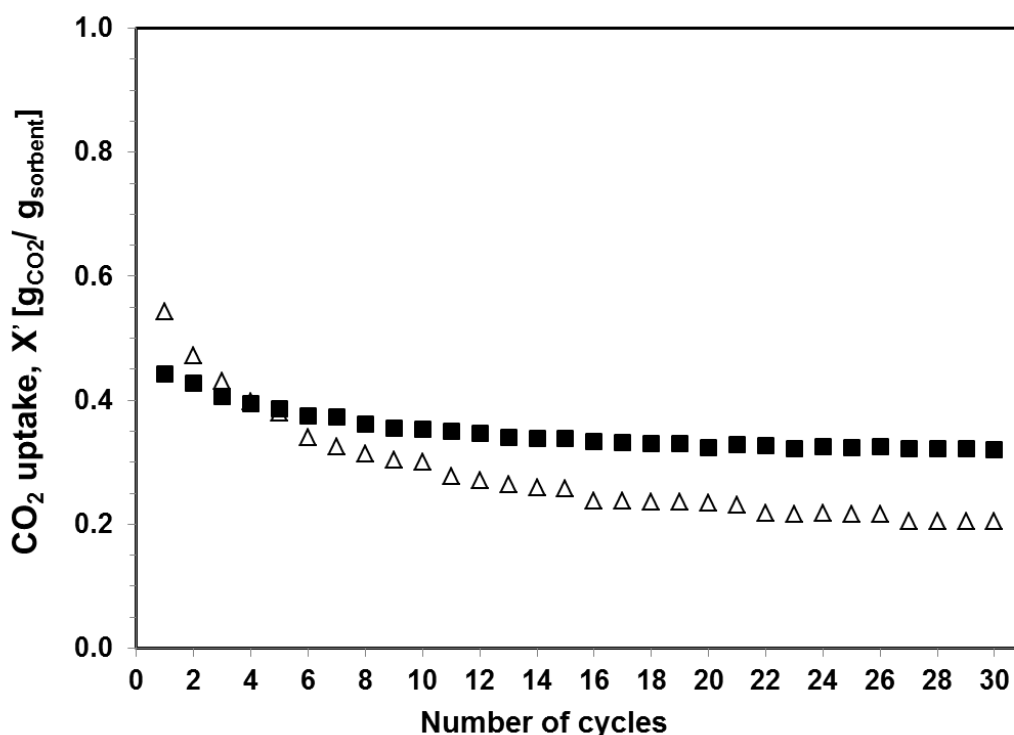
Figure 2. CO_2 uptake over 30 cycles for synthetic and natural sorbents obtained from TGA measurements. The carbonation and calcination temperature was 750 °C: ($\blacksquare$) $Ca(NO_3)_2$ precipitated using Na_2CO_3 at pH 7.0 and ($\triangle$) Havelock limestone.

cycle number two, the sorbent co-precipitated from $Ca(NO_3)_2$ at pH 7.0 significantly outperformed limestone with respect to (i) CO_2 uptake, (ii) CaO conversion and (iii) decay rate. On the other hand, the sorbent precipitated from $Ca(NO_3)_2$ at pH 9.7 is, with respect to CO_2 uptake after 10 cycles, the worst of all the sorbent derived using Na_2CO_3 as the precipitation agent. Thus, for precipitation using $Ca(NO_3)_2$ as the calcium precursors, the pH value is a crucial synthesis parameter whereas, for precipitation using $Ca(C_2H_3O_2)_2$ as the calcium precursors, the influence of the pH value on the performance of the sorbents appears to be small.

To investigate the long-term stability of the synthetic sorbent which showed the best CO_2 capture characteristics over 10 cycles, 30 cycles of repeated calcination and carbonation were performed in a TGA. From Fig. 2 it can be seen that the synthetic sorbent possesses an almost constant CO_2 uptake from cycle number 10 onwards, whereas the CO_2 uptake of limestone continuously decreases over 30 cycles. After 30 cycles the CO_2 uptake capacity of the best synthetic sorbent and Havelock limestone are 0.32 and 0.20 g CO_2/g sorbent, respectively. Thus, the synthetic sorbent exceeds the performance of limestone by more than 50 %.

The BET surface area, pore volume and mean pore radius determined from N_2 adsorption isotherms are summarized in Table 1. The material synthesized using $Ca(NO_3)_2$ as the calcium precursor and NH_3 as the precipitation agent shows the highest surface area and pore volume, independent of the pH value at which the precipitation was performed. Using Na_2CO_3 as the precipitation agent and $Ca(NO_3)_2$ or $Ca(C_2H_3O_2)_2$ as the calcium precursor resulted in significantly smaller BET surfaces areas and pore volumes. Only the use of $Ca(NO_3)_2$ as the calcium precursor and precipitating with Na_2CO_3 at pH 7.0 resulted in reasonably high surface areas and pore volume, *i.e.* 14.35 m^2/g and 0.21 cm^3/g, respectively.

Table 1. BET surface area, total pore volume (determined using BJH analysis) and mean pore radius of different synthetic and natural sorbents.

Sorbent	BET surface area $[m^2/g]$	Pore volume $[cm^3/g]$	Pore radius $[nm]$
$Ca(C_2H_3O_2)_2$, pH 7, Na_2CO_3	5.9	0.04	1.84
$Ca(NO_3)_2$, pH 7, Na_2CO_3	14.35	0.27	3.36
$Ca(NO_3)_2$, pH 7, NH_3	137.12	0.21	3.36
$Ca(C_2H_3O_2)_2$, pH 9.7, Na_2CO_3	3.26	0.01	1.83
$Ca(NO_3)_2$, pH 9.7, Na_2CO_3	1.81	0.02	4.05
$Ca(NO_3)_2$, pH 9.7, NH_3	168.79	0.63	8.23
Havelock limestone	14.19	0.120	NA

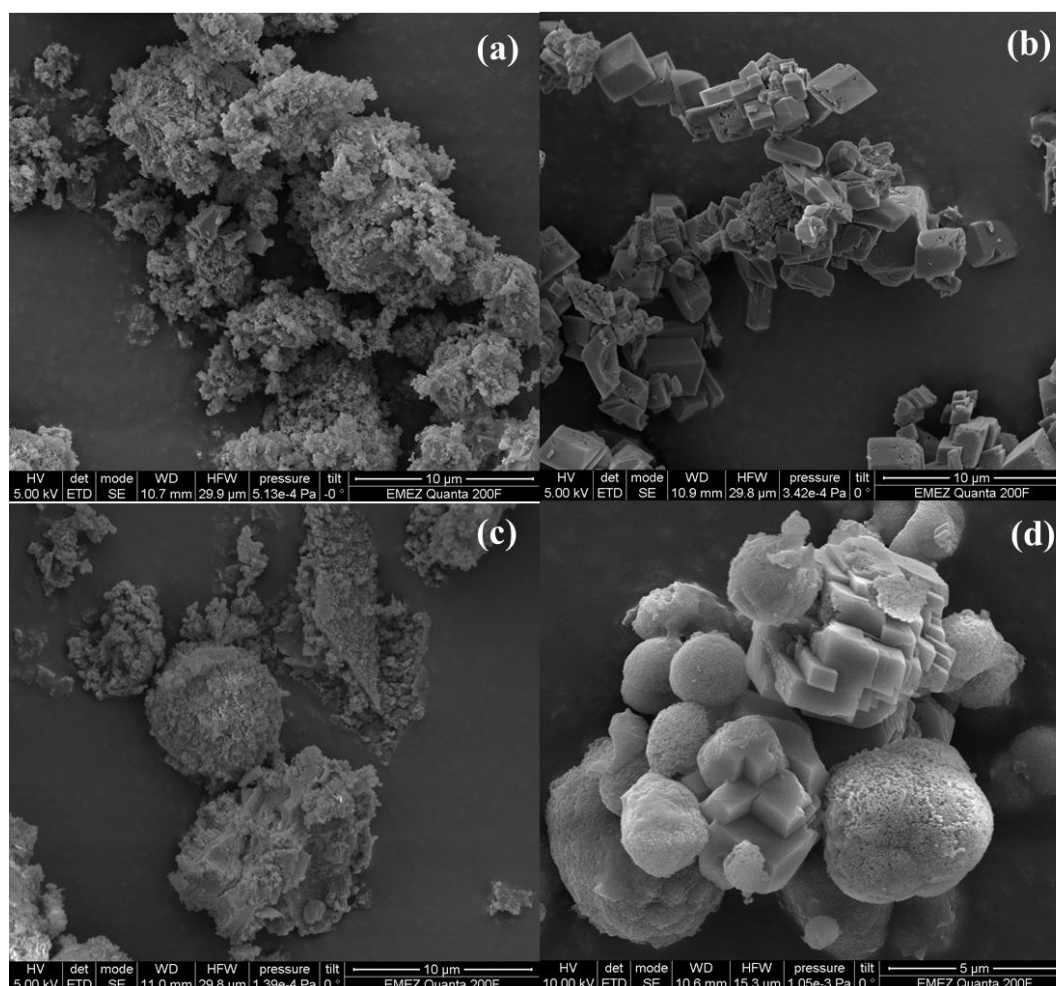**Figure 3.** Images showing the crystal morphology of the freshly precipitated sorbents: (a) $Ca(C_2H_3O_2)_2$ using Na_2CO_3 at pH 7.0, (b) $Ca(C_2H_3O_2)_2$ using Na_2CO_3 at pH 9.7, (c) $Ca(NO_3)_2$ using Na_2CO_3 at pH 7.0 and (d) $Ca(NO_3)_2$ using Na_2CO_3 at pH 9.7.
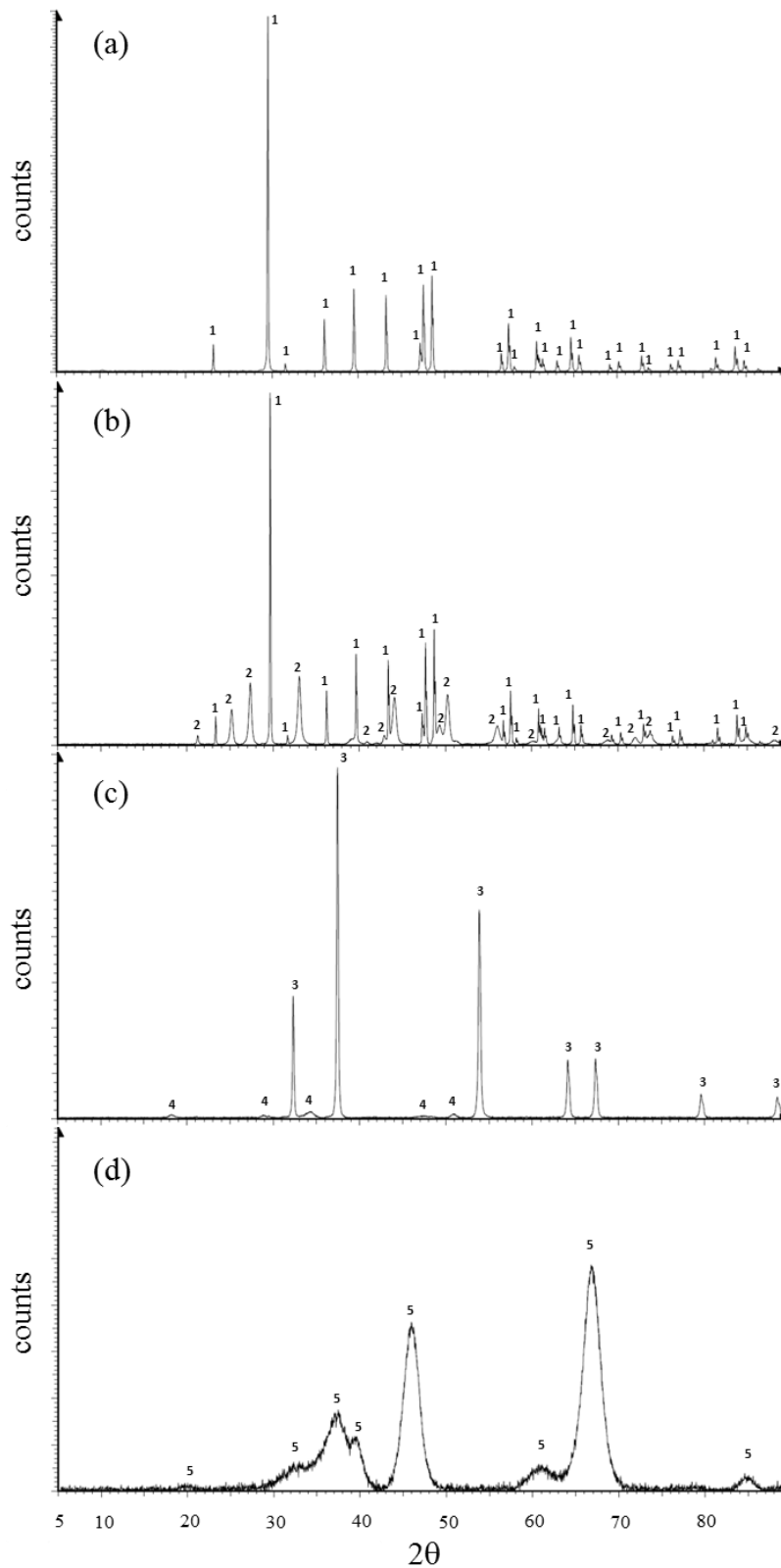
Figure 4. XRD pattern of sorbents, '1' calcite, $CaCO_3$, '2' vaterite, $CaCO_3$, '3' lime, CaO, '4' portlandite, $Ca(OH)_2$ and '5' aluminium oxide, Al_2O_3: (a) $Ca(C_2H_3O_2)_2$ co-precipitated with $Al(NO_3)_2$ using Na_2CO_3 at pH 9.7, dried sample (b) $Ca(NO_3)_2$ co-precipitated with $Al(NO_3)_2$ using Na_2CO_3 at pH 9.7, dried sample, (c) $Ca(C_2H_3O_2)_2$ co-precipitated with $Al(NO_3)_2$ using Na_2CO_3 at pH 7.0, sample calcined at 800 °C and (d) $Al(NO_3)_2$ using Na_2CO_3 at pH 7.0, sample calcined at 800 °C.

In agreement with observations made for the CO_2 uptake characteristics, it was found that for precipitation using Na_2CO_3 and $Ca(C_2H_3O_2)_2$ as the calcium precursor the pH value had only a small influence on the surface area and pore volume of the sorbents, whereas using $Ca(NO_3)_2$ as the calcium precursors the pH value at which the precipitation was performed markedly influenced the surface area and pore volume of the sorbent obtained.

SEM images showing the crystal morphology of the precipitated sorbents are given in Fig. 3. Figure 3(b) shows clearly that $CaCO_3$ is precipitated in the form of cubic calcite crystals for the case that $Ca(C_2H_3O_2)_2$ was used as the calcium precursor and the precipitation was performed with Na_2CO_3 at pH 9.7. The average size of the calcite crystals was 2.08 μm (based on the analysis of 10 crystals). On the other hand, if the precipitation was performed at a pH value of 7.0, as shown in Fig. 3(a), no well-defined crystals could be observed. Turning now to the precipitation of $Ca(NO_3)_2$ with Na_2CO_3, it can be seen from Fig. 3(d) that if the precipitation was performed at pH 9.7, $CaCO_3$ was crystallized in the form of spherical vaterite and cubic calcite. Again, for precipitation at a pH value of 7.0, the crystals obtained were less-defined and a visual identification of the $CaCO_3$ polymorph was not possible, see Fig. 3(c).

X-ray diffraction (XRD) patterns of both dried and calcined sorbents are shown in Fig. 4. The XRD pattern of the sorbent prepared using $Ca(C_2H_3O_2)_2$ as the calcium precursor and precipitated with Na_2CO_3 at pH 9.7 is given in Fig. 4(a); it is clear that $CaCO_3$ is precipitated entirely in the form of cubic calcite. On the other hand, when the precipitation was performed at pH 7.0, $CaCO_3$ was precipitated in the form of both vaterite and calcite, although predominantly in the form of calcite. The XRD pattern of the precipitate prepared using $Ca(NO_3)_2$ as the calcium precursor and precipitated with Na_2CO_3 at pH 9.7 is shown in Fig. 4 (b). The XRD pattern in Fig. 4(b) demonstrates that when the precipitation was performed at pH 9.7 vaterite and calcite are formed. Similar XRD patterns were obtained when the precipitation was performed at pH 7.0. Upon calcination, $CaCO_3$ decomposes into CaO, independent of the initial $CaCO_3$ polymorph which is shown in Fig. 4(c). It is worth mentioning that when Na_2CO_3 was used as the precipitation agent, no Al-compound could be observed in the XRD pattern, irrespective of the calcium precursor and the pH value at which the precipitation was performed. The XRD pattern of a calcined precipitate obtained by adding Na_2CO_3 to a solution containing only $Al(NO_3)_3$ until a pH value of 7.0 was obtained is shown in Fig. 4(d). From Fig. 4(d) it can be concluded that amorphous Al_2O_3 is present in the calcined sorbents. The formation of amorphous $Al(OH)_3$ would explain the absence of any peaks for aluminium compounds in the XRD pattern of the co-precipitated sorbents.

Discussion

The XRD, SEM and N_2 adsorption measurements demonstrate convincingly that both the chemical composition and the morphology of the precipitates are strongly influenced by (i) the calcium precursor, (ii) the precipitation agent and (iii) the pH value at which the precipitation was performed. For example, using $Ca(C_2H_3O_2)_2$ as the calcium precursor and precipitating with Na_2CO_3 at pH 7.0 yielded $CaCO_3$ in the form of cubic calcites, whereas precipitating $Ca(NO_3)_2$ with Na_2CO_3 at pH 9.7 yielded $CaCO_3$ in the form of both spherical vaterite and cubic calcite. At pH 7.0 the precipitates were predominantly calcite with some vaterite, irrespective of the calcium precursor. However, based on the acquired SEM images of the dried precipitates, only precipitation at pH 9.7 results in well-defined and clearly identifiable crystals shapes. Comparing the morphology of the precipitates determined using XRD and SEM with the corresponding surface areas and pore volume it seems that ill-defined crystals leads to a higher surface area and pore volume in the calcined sorbent. This may be explained by the fact that the crystals themselves are non-porous and the porosity in the macroscopic sorbent is only obtained due to voids forming between sintered crystals. For

smaller and ill-defined crystals, as obtained for co-precipitation performed at pH 7.0, the macroscopic particles could possess a higher porosity and, thus, pore volume owing to the smaller "building-blocks". Nonetheless, the high surface area and pore volume of 14.35 m^2/g and 0.27 cm^3/g, respectively, of the sorbent synthesized at pH 7.0 using $Ca(NO_3)_2$ as the calcium precursor and Na_2CO_3 as the precipitation agent stands out. The sorbent synthesized at pH 7.0 using $Ca(C_2H_3O_2)_2$ as the calcium precursor and Na_2CO_3 as the precipitation agent showed a significantly lower surface area and pore volume of only 5.9 m^2/g and 0.019 cm^3/g, respectively. Currently, we cannot provide an explanation for this behaviour, since the XRD patterns and SEM images of the two sorbents precipitated with Na_2CO_3 at pH 7.0 are very similar. Comparing the BET surface areas and pore volumes of the synthesized sorbents with the cyclic CO_2 capture capacity demonstrates convincingly that the sorbent with the highest surface area and pore volume provides the highest CO_2 uptake. The CO_2 uptake of the sorbent synthesized using $Ca(NO_3)_2$ as the calcium precursor and precipitated with Na_2CO_3 at pH 7.0 shows a CO_2 uptake of 0.32 g CO_2/g sorbent after 30 cycles, comparing favourable with limestone which showed a CO_2 uptake capacity of 0.20 g CO_2/g sorbent after 30 cycles. It is assumed that the inert Al_2O_3 matrix of the synthetic sorbent reduces the extent of pore closure due to $CaCO_3$ sintering [10,17].

Based on the hypothesis that the kinetically controlled part of the carbonation reaction ceases once the volume available in the small pores (d_p < 200 nm) is filled with the newly formed $CaCO_3$, Pacciani et al. [10] proposed the following equation correlating the pore volume for pores with d_p < 200 nm and the CO_2 uptake, X', in g CO_2/g sorbent, viz.

$$X' = 44/56 \cdot V_0 \cdot \rho_{CaO} / (1/Z-1) \quad (2)$$

where ρ_{CaO} = 3.32 g/cm^3, Z = 0.46 and V_0 are the crystal density of CaO, the ratio of the molar volumes of CaO and $CaCO_3$, and the volume contained in pores with d_p < 200 nm, respectively. Applying Eq. (2) for the best synthetic sorbent considered here, i.e. $Ca(NO_3)_2$ precipitated with Na_2CO_3 at pH 7.0 gives, for the 1st cycle, X' = 0.60. The experimental value for X' was 0.44. Thus, for the best sorbent synthesized in this study, Eq. (2) over-predicts the CO_2 uptake. On the other hand, Eq. (2) significantly under-predicts the CO_2 uptakes of the other sorbents. Currently we do not have an explanation as to why Eq. (2) holds only for some sorbents [10].

Based on XRD and SEM measurements it is clear that the Al_2O_3 support of the sorbent is amorphous. Furthermore, we could not observe the formation of any Ca-Al mixed oxides, such as mayenite ($Ca_{12}Al_{14}O_{33}$). Pacciani et al. [10] and Li et al. [11] reported the formation of mayenite in Ca-Al-based sorbents prepared using a hydrolysis method. It may be possible that the formation of mayenite only occurs at higher calcination temperatures. The fact that sorbents synthesized using NH_3 as the precipitation agent, despite their high surface areas and pore volumes, did not show any CO_2 uptake can be explained readily by the fact that only amorphous $Al(OH)_3$ was precipitated out under these conditions. These precipitation characteristics were confirmed by XRD and SEM measurements.

Conclusions

The co-precipitation technique was employed to synthesize Ca-based, Al_2O_3-stabilized sorbents for CO_2 capture. The chemical composition, morphology and the cyclic CO_2 uptake of the synthesized sorbents were strongly influenced by (i) the calcium precursor, (ii) the precipitation agent and (iii) the pH value at which the precipitation was performed. Sorbents which were synthesized using $Ca(NO_3)_2$ as the calcium precursor, and precipitated with Na_2CO_3 at pH 7.0 showed the best cyclic CO_2 uptake capability: 0.32 g CO_2/g sorbent after 30 cycles of calcination and carbonation, which is ~ 50 % higher than for limestone. It was

found that precipitates which showed small and ill-defined crystal shapes produced the highest surface area and pore volume in the calcined sorbents. In turn, the synthetic sorbent with the highest pore volume possessed the best cyclic CO_2 capture characteristics.

Acknowledgement

References

[1] IPCC (2007). Climate Change 2007. Fourth Assessment Report, Intergovernmental Panel on Climate Change (IPCC), U.N., available on www1.ipcc.ch/ipccreports/ar4-wg1.htm

[2] Singh, D., Croiset, E., Douglas ,P.L., Douglas, M.A., "Techno-economic study of CO2 capture form an existing coal-fired power plant: MEA scrubbing vs. O-2/CO2 recycle combustion", *Energy Conv. & Manag*. 44: 3073-3091 (2003).

[3] MacKenzie, A., Granatstein, D.L., Anthony, E.J., Abanades, J.C., "Economics of CO_2 capture using the calcium cycle with a pressurized fluidized bed combustor", *Energy & Fuels*, 21: 920-926 (2001)

[4] Fennell, P.S., Pacciani, R., Dennis, J.S., Davidson, J.F., Hayhurst, A.N., "The effect of repeated cycles of calcination and carbonation on a variety of different limestones, as measured in a hot fluidized bed of sand", *Energy & Fuels* 21: 2072-2081 (2007).

[5] Silaban A., Narcida, M., Harrison, D.P., "Characteristics of the reversible reaction between CO_2(g) and calcined dolomite", *Chem. Eng. Comm*. 146: 149-162 (1996).

[6] Abanades, J.C., Alvarez, D., "Conversion limits in the reaction of CO_2 with lime", *Energy & Fuels* 17: 308-315 (2003).

[7] Wang, J., Anthony, E.J., "On the decay behaviour of the CO_2 adsorption capacity of Ca-based sorbents", *Ind. & Eng. Chem. Res*. 44: 627-629 (2005).

[8] Sun, P., Lim, C., Grace, J.R., "Cyclic CO_2 capture by limestone-derived sorbent during prolonged calcination/carbonation cycling", *AIChE J*. 54: 1668-1677 (2008).

[9] Alvarez, D., Abanades, J.C., "Determination of the critical product layer thickness in the reaction of CaO with CO_2", *Ind. & Eng. Chem. Res*. 44: 5608-5615 (2005).

[10] Pacciani, R., Müller, C.R., Davidson, J.F., Dennis, J.S., Hayhurst, A.N., "Synthetic Ca-based solid sorbents suitable for capturing CO2 in a fluidized bed", *Can. J. Chem. Eng*. 86: 356-366 (2008).

[11] Li, Z.S., Cai, N.S., Huang, Y.Y., Han, H.J., "Synthesis, experimental studies and analysis of a new calcium-based carbon dioxide sorbent", *Energy Fuels* 19: 1447-1452 (2005).

[12] Pacciani, R., Müller, C.R, Dennis, J.S., Davidson, J.F., Hayhurst, A.N., "How does the concentration of CO_2 affect its uptake by a synthetic Ca-based solid sorbent?", *AIChE J*. 54: 3308-3311 (2008).

[13] Wu, S.F., Li, Q.H., Kim, J.N., Yi, K.B., "Properties of a nano CaO/Al2O3 CO2 sorbent", *Ind. & Eng. Chem. Res*. 47: 180-184 (2008).

[14] Brunauer, S., Emmett, P.H., Teller, E., "Adsorption of gases in multimolecular layers", *J. Am. Chem. Soc*. 60: 309-319 (1938).

[15] Barrett, E.P., Joyner, L.G., Halenda, P.P., "The determination of pore volume and area distributions in porous substances. I Computations from nitrogen isotherms", *J. Am. Chem. Soc*. 73: 373-380 (1953).

[16] Grasa, G.S., Abanades, J.C., "CO2 capture capacity of CaO in long series of carbonation and calcination cycles", *Ind. Eng. Chem. Res*. 45: 8846-8851 (2006).

[17] Sun, P, Grace, J.R., Lim, C.J., Anthony, E.J., "The effect og CaO sintering on cyclic CO2 capture in energy systems", *AIChE J*. 53: 2432-2442 (2007).