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In-situ XRD studies of dolomite based CO₂ sorbents

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Abstract

Calcined dolomite (a CaOMgO material derivative of the natural mineral dolomite) has the potential as a CO₂ sorbent working at high temperatures (500–650 °C) in processes like post combustion carbonate-looping, or in sorbent enhanced reactions such as sorbent-enhanced water-gas shift (SEWGS) or sorbent-enhanced reforming (SER). However, deactivation and performance loss is inevitable and much effort has been aimed towards understanding and improving solid sorbents for various applications. This work presents a study of deactivation trends of calcined dolomite and Zr-modified versions of calcined dolomite that appears to possess better cyclic properties at rapid sorption-desorption cycling (which is a likely conditions in a real process using a CFB reactor). Surface area measurements, thermogravimetric analyses (TGA), fixed bed reactor studies, *in-situ* XRD and *in-situ* IR methods carried out at 600°C in a gas containing 1–2vol% steam in 10% CO₂ have been conducted to obtain fundamental information about the de-activation mechanisms taking place.

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1. Introduction

Reduction of anthropogenic CO₂ emissions is important in order to mitigate global warming. One main source of CO₂ emissions is power production from fossil fuels, and huge efforts have been carried out to enable large scale solvent based CO₂ capture processes that can be retrofitted to existing power plants. These will likely be based on

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water solutions of amines [1]. Other technological solutions for removing CO₂ are e.g. based on membranes or solid sorbents but are at present less mature than solvent based processes. However, many of these show promising economical potentials as exemplified by the high temperature solid looping sorbent process "Calcium Looping", CaL, and "Sorption enhanced steam methane reforming", SE-SMR, which both are assessed by techno-economic evaluations to have a reduced efficiency penalty compared to standard amine based processes [2,3,4,5].

The CaL process is a post combustion technology that is based on the idea that CaO(s) is reacting with CO₂(g) to CaCO₃(s) hence removing gas phase CO₂ from a gas mixture, see eq. 1 below.



CaL has received large interests during the last 10-15 years, with several small (10-100 kW) and medium sized units (1-2 MW) demonstrated [6,7], but there is still a concern connected to the cost, and particular, the lifetime of the sorbent powder(lime stone).

Different from the CaL, but with essential similarities concerning sorbent use, is the SE-SMR. SE-SMR is a process for improved hydrogen production with simultaneous CO₂ capture since the reactions are driven towards H₂ as CO₂ is captured by the solid sorbent (typically CaO or calcined dolomite, CaOMgO). The hydrogen, which has a purity of about 97-98 % if CaO is the active sorbent component, may then be further purified for the hydrogen market or burned for electricity generation.

The CaL and SE-SMR processes are suited for circulating fluidized bed (CFB) reactor systems [6,7,8]. The most essential features of a CFB CaL-process and the SE-SMR processe are shown schematically below:

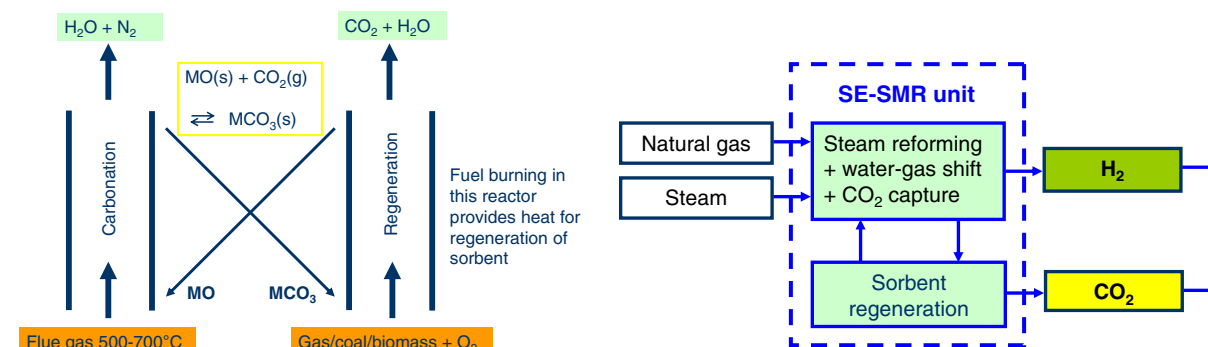


Figure 1. Left: Schematic drawing of the Ca-looping process, and right: Principle of the sorption enhanced steam methane reforming process

As in all processes that utilize powders sorbent deactivation in the CaL and SE-SMR processes are inevitable. As a consequence of the somewhat limited lifetime of easily accessible natural minerals such as lime and dolomite, much research has been aimed towards making new artificial (nano)materials. However, due to CaO's favorable thermodynamic properties combined with relatively fast reaction rates with CO₂ most recent research has been focused on making materials that have CaO as the active phase, possibly fixed in a suitable matrix. Various strategies for preparing improved CaO based materials are e.g.: Thermal pre-treatments of lime [9], hydration of lime [10], doping CaO by KMnO₄ [11], dispersion of CaO on various supports like e.g. Ca₁₂Al₁₄O₃₃ or CaTiO₃ [12, 13], or co-precipitation of Ca with other elements (M) like Cr, Mn, Co, Cu, or Ce, for a nominal composition of Ca_{0.9}M_{0.1}O_x [14], or CaO on MgO mixed with Ca₉Al₆O₁₈ [15], or CaCeZrO_x [16]. Lately, we tried to deposit Ti-, Zr-, and Al-nanoparticles on calcined dolomite in order to stabilize and improve cyclic performance without any real success [17]. However, the idea was followed further and by focusing on other Zr-sources, different loaded amounts, and other experimental conditions we hoped to improve the materials. In addition we coupled this work with studies of deactivation trends of calcined dolomite and applied several quite different techniques during the experimental work. After material preparations we used N₂ BET and micropore volume measurements to assess surface and pore volumes, powder XRD to investigate new phases present after Zr-modifications, thermogravimetric analyses (TGA) to measure CO₂ uptake capacities of the sorbents, dual fixed bed reactor for measuring CO₂ breakthrough curves and to have an improved control of flow and reactivity compared to normal TGA analyses. The fixed bed rig has also

been used to study rapid adsorption-desorption cycling performance, which it is very suited for. In addition we have performed *in-situ* XRD and *in-situ* DRIFTS FTIR characterization of fresh and aged materials under realistic conditions, including cycling between sorption and desorption of CO₂, in order to unravel fundamental aspects of the performance and decay trends. All sorption experiments for all methods have been at 600 °C using a 1-2% steam in 10% CO₂ balanced in N₂ gas mixture. Regeneration was carried out using N₂ gas at 850 or 900 °C.

2. Experimental

The starting material in this work is the natural mineral dolomite (CaMg(CO₃)₂) from Seljelid, Norway. In order to prepare dolomite as an acceptor for CO₂ the oxide version was formed by heat treatment (calcination) of the mineral for 12 hours at 900°C in 10% H₂. This procedure transformed the dolomite into an oxide form that can be termed CaOMgO, or calcined dolomite (there is close to a 1:1 ratio of Mg and Ca). Two other Zr modified samples, with Zr nominal loadings of 0.5wt.% and 1wt.%, were made by impregnating the calcined dolomite with Zr-nitrate in line with incipient wetness methods. After impregnation the samples were calcined in air for 15 hours at 900 °C. Higher loadings were also made but these were inferior but are mentioned later (*vide infra*).

BET surface and micropore volume were measured by nitrogen adsorption at 77K for all samples using a BELSORP Mini instrument.

In order to assess the cyclic CO₂ uptake/desorption capacity and kinetics, we studied the materials by Thermo Gravimetric analysis (TGA) and a fixed bed rig for CO₂ breakthrough measurements. Not all materials were tested in both apparatuses. The gas composition used in these instruments for testing the materials were in all cases a mix of 10vol.% CO₂ and 1vol.% H₂O balanced with N₂. This was obtained by bubbling the 10% CO₂ in N₂ mix through water cooled to about 11°C with a total pressure of 1 atm. The TGA experiments were carried out in a Netzsch STA449 F1 instrument using the following conditions: First, the temperature was raised to 900 °C at 10°C/min in N₂. The temperature was kept constant for 3h before it was lowered to 600 °C at a rate of 10 °C/min. After 5 minutes at 600 °C in N₂ the sample was exposed to the reactive gas for 20 minutes. After the sorption step the temperature was raised to 900 °C for 30 minutes in pure nitrogen in order to regenerate the sorbent. Then the temperature was lowered to 600 °C. The steps after the initial 3h at 900 were repeated 60 times. The outlet gas was analyzed by an online mass spectrometer (MS) and an in-house developed Labview program controlled the whole gas feeding sequence automatically.

In order to assess further the CO₂ uptake/desorption capacity and kinetics, we tested the materials in a fixed bed reactor and measured breakthrough curves. Figure 2 shows schematically the principle of the dual fixed bed test rig and a typical raw data output.

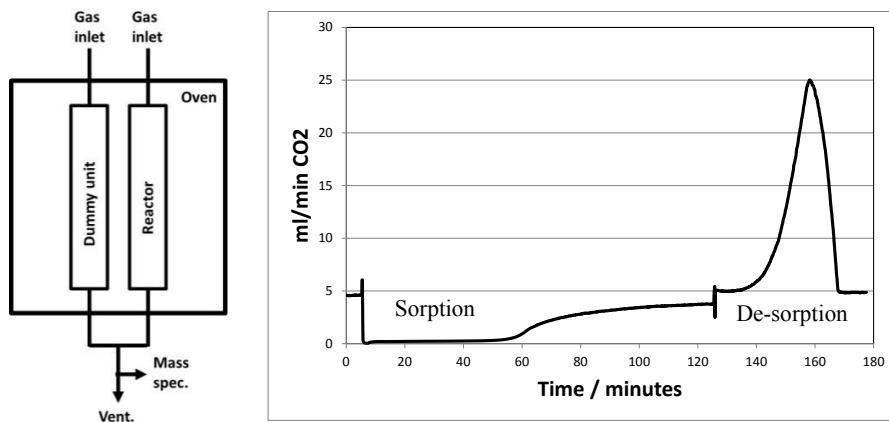


Figure 2. Left: Principle of the breakthrough rig and example of breakthrough curve. Right: The black line is the MS CO₂ signal (actually the m/z=44 signal)

The inner diameter of the reactor tubes were 1 cm and we applied a 4 cm high bed. The amount sorbent was typically between 2.3 and 2.4 grams. The reactor contained the sorbent while the dummy reactor contained quartz. Temperatures in the bed were measured at four points along the bed height. The gas flows were 50ml/min through both reactors, one stream was pure N₂ and the other was 10% CO₂ in N₂ saturated with H₂O at 10-11°C, i.e. app. 1% water similar to the TGA experiments. The outlet gas was analyzed by an online MS and an in-house developed Labview program controlled the whole sequence automatically. In the initial phase of a test the reactor tubes were heated to 600 °C by an electrically furnace. Pure N₂ was entering the reactor with the sorbent while the CO₂ containing gas entered the dummy reactor. At this stage the continuous CO₂ MS signal (m/z = 44) shows the intensity of 5 ml/min CO₂ (the first minutes of the MS trace above). After ten minutes at 600 °C a valve switched so that the CO₂ containing gas enters the reactor tube with sorbent and the pure N₂ gas enters the dummy reactor. The valve switch is seen by a spike in the MS signal. During sorption CO₂ is reacting with the sorbent and is removed from the gas phase and the MS signal from CO₂ (m/z = 44) declines. After some time with adsorption of CO₂ the MS signal starts to increase termed a CO₂ breakthrough, i.e. the sorbent does not absorb all the CO₂ entering the powder bed. Further on in time, the MS signal from CO₂ rises almost to the initial level observed before the sorption took place. Other reaction conditions, like e.g. higher partial pressure of CO₂, more added steam, or other temperatures will change this picture but the general features of the curve would still be the same. After a predetermined time (10 or 120 minutes as in our cases reported here) with CO₂ gas over the sorbent the gases are switched again and the temperature was increased to 850 °C. During the heating period in N₂ (regeneration) the sorbent released the previously absorbed CO₂ and this is indicated as the de-sorption region in the figure. After desorption was complete a cycle had passed. Experiments were done with varying bed heights, reaction times and flows in order to ensure reliable and proper data. In one experiment reported below the adsorption time was 120 minutes and 13 cycles were carried out, while for the other experiments 90 cycles were carried out with 10 minutes adsorption times. In these 10 minutes adsorption cycle experiments, there was in practice no CO₂ breakthrough when switching over to regeneration conditions and it took about a week to complete all 90 cycles. The adsorption capacity was evaluated using an in-house developed Excel macro software. The conversion of sorbent is also evaluated and is defined as the moles CO₂ adsorbed pr. mol CaO unit in the sample and is based on the following estimate of total capacity. Since the molecular weight of CaOMgO (calcined dolomite) is 96 g/mol CaO constitutes 100%* 56/96=71% of the weight. 1 gram sorbent contains around 710 mg CaO which corresponds to 12.7 mmol and is also the amount CO₂ possible to adsorb if given enough time.

The X-ray diffraction (XRD) measurements were performed on a PANalytical Empyrean diffractometer. The system is equipped with a PIXcel^{3D} solid state detector. The measurements were carried out in reflection geometry using CuKα₁ radiation ($\alpha = 1.54060 \text{ \AA}$) and a step size of 0.013 degrees. An Anton Paar XRK 900 *in-situ* high-temperature (25-900°C) and high pressure (1-10 bar) reactor cell coupled to an automated gas switching system was used for the *in-situ* XRD experiments. The pressure was 1 atm. and the feed gas employed was a 10% CO₂ in N₂ mix saturated with H₂O at 10-11°C, i.e. app. 1% water, for a total flow 100 ml/min. Ca. 150-160 mg sample powder was used for each experiment. For the plotting and analyses of the *in-situ* XRD the reflection at $2\theta=29.3^\circ$ for CaCO₃ and at $2\theta=37.2^\circ$ for CaO. The experimental reaction condition protocol is schematically shown below.

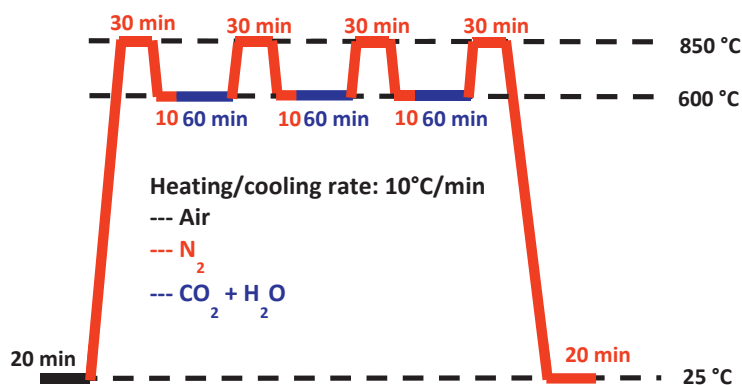


Figure 3. The reaction condition protocol for the *in-situ* XRD experiments.

FTIR spectra were recorded on a Bruker Vertex 70 equipped with a MCT-detector, DRIFTS-cell (HVC-DRP-2), temperature controller, and Praying-Mantis from Harrick. The spectra were recorded at a resolution of 4 cm^{-1} , and each spectrum is the average of four scans. All spectra were collected in reflectance mode, and we used a spectrum of the solid samples under pure N_2 collected just prior to their exposure to the gas mixture as background spectra. The solid samples were loaded into the sample cup and heated under flowing N_2 according to the same temperature program as used for PXRD. When the temperature was stable at 600°C , we carefully switched from a pure N_2 -flow to a flow of 10% CO_2 diluted in N_2 that was bubbled through distilled H_2O before it entered the DRIFTS-cell. Due to the dead volume in the gas-feeding system and DRIFTS-dome, we define $t = 0$ when the first visible bands appeared in the spectra.

3. Results and discussion

3.1. Deactivation studies of calcined dolomite

Table 1. Material summary for deactivation studies of calcined dolomite

Type	BET area, m^2/g	Micropore volume, cm^3/g
Calcined dolomite	19.2	0.26
Wet-90, 90 cycles wet CO_2	9.6	0.18
Wet-13, 13 cycles wet CO_2	9.2	0.15

The fixed bed experiments were carried out such that the total CO_2 capacity that had been adsorbed by 90 short cycles was about the same as in 13 long adsorption cycles. The adsorbed amounts pr. cycles for these two experiments are shown in figure 4. The total CO_2 uptake was 77 mmol for the 90 cycle experiment and 83 mmol for the 13 cycle experiment. The total CO_2 uptake, BET surface and micropore volume of these used materials were therefore quite similar.

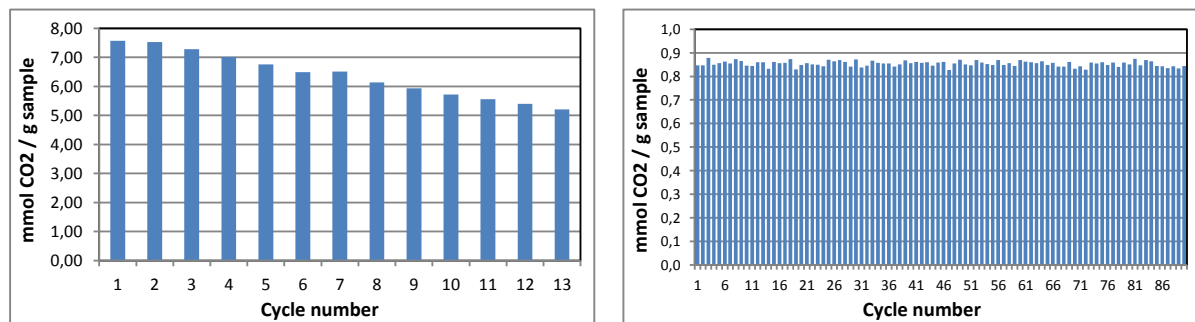


Figure 4. Left: 13 cycles wet CO_2 with conversion going from about 59% to ~40%. Right: 90 cycles wet CO_2 with conversion about 7 %

The fixed bed experiments clearly shows that by employing most of the available capacity in each cycle a clear deactivation trend is observed with a steady reduction in the cyclic capacity for each cycle, which is in contrast to the data from the short adsorption time experiment as the performance is apparently quite stable for the 90 cycles.

Representative SEM images of the used samples are shown below but did not give any hints to the different trends. Hence the deactivation profile during long cycle experiments is likely not as a result of big morphological changes.

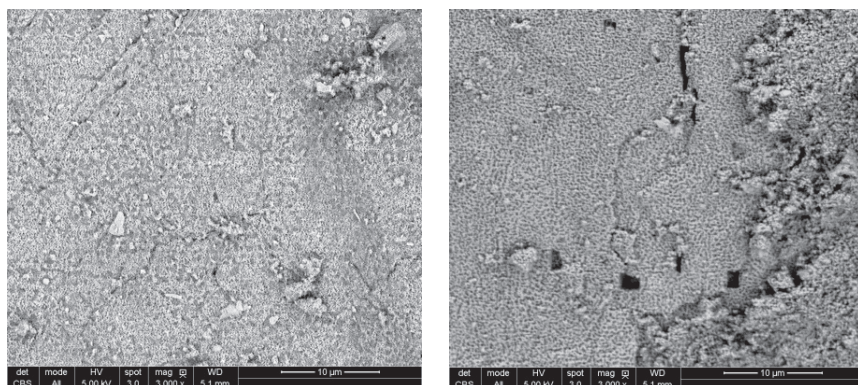


Figure 5. SEM images after 13 long ad-des cycles (left) and 90 short ad-des cycles. The SEM images show that there are no apparent big differences in morphology for the samples.

In an attempt to further understand the differences in performance depending upon the adsorption time *in-situ* XRD experiments were carried out on the two used samples and a calcined unused dolomite. Intensities of selected reflections (as described in part 2) are plotted as histograms. Scan number is a complete XRD data set and is a sum of several scans again.

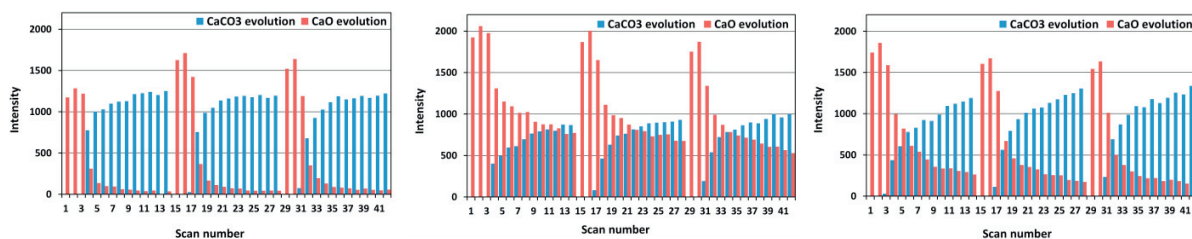


Figure 6. *in-situ* XRD plot showing the CaCO₃ and CaO evolution through 3 ad-des cycles. Left: Calcined dolomite. Middle: After 13 cycles wet CO₂. Right: After 90 cycles wet CO₂.

As one can see the unused calcined dolomite shows much faster and complete reaction with CO₂ to CaCO₃. The 90 cycle material has been deactivated compared to the unused calcined dolomite but not as much as the long cycle material. This is complementary circumstantial evidence indicating that applying a smaller adsorption capacity leads to a longer lifetime, even at about the same captured CO₂ amounts. This might also well be similar in other sorbents and is not really surprising considering that the less CO₂ adsorbed the less strain on the materials during the reactions.

3.2. Improving performance of calcined dolomite by Zr impregnation

Understanding deactivation of sorbents for an eventual improvement has been an important topic for long time. Based upon the idea that an added element might act as a promoter we impregnated the calcined dolomite with various loading of Zr. The Zr modified materials were made with the aim of improving cyclic stability, however, by impregnating a compound like calcined dolomite, which has a relative small surface area, the available surface area for reactions might become lower. Table 2 below shows this effect but it is not until 5wt.% Zr loading the BET and micropore volume decrease significantly. At 10 wt.% Zr loading the effect is similar to the 5wt.% material. Neither of these will be further described here as they had low performance compared to the other samples.

Table 2. Zr modified material summary

Type	BET area, m ² /g	Micropore volume, cm ³ /g
0.5 wt.% Zr	16.1	0.24
1 wt.% Zr	11.7	0.10
5 wt.% Zr	5.7	0.06

The impregnated samples were analyzed with powder XRD and for all materials with added Zr there had been formed an extra perovskite phase that could be e.g. CaZrO₃. This phase is only a minor component and has no significant reactivity towards CO₂ but it may be detrimental to the sorption process anyway. In figure 7 below a typical XRD is shown.

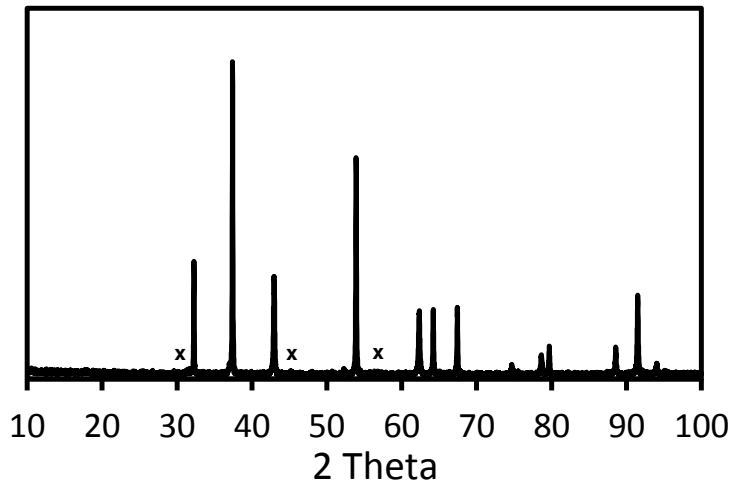


Figure 7. XRD data for the 1 wt.% Zr sample. There are small reflections that are identified as a perovskite phase and could maybe be e.g. CaZrO₃ (some reflections are marked with x). This phase is seen in all samples impregnated with Zr. Other peaks are from CaO (the active phase) and MgO.

In order to assess basic cyclic sorption performance we tested the materials in a thermogravimetric analyses instrument (TGA) and a fixed bed reactor as described in section 2. Below are the TGA data for the 0.5 wt.% and 1 wt.% samples listed in Table 2. The 5 wt.% Zr sample is not shown due to significant less CO₂ uptake capacity (around stable 11-12 wt.%) and at 10 wt.% the capacity is further down to about 6-7 wt.% CO₂ uptake.

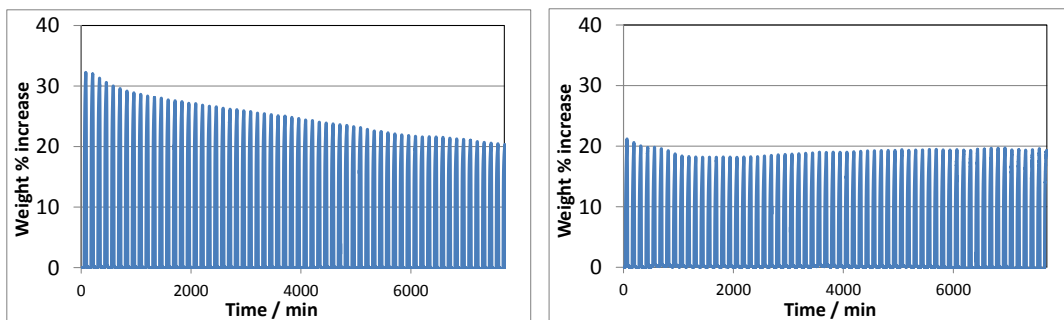


Figure 8. TG data for the 0.5 wt.% Zr (left), and the 1% Zr (right) modified materials. Adsorption at 600°C using 10% CO₂, 1% H₂O balanced in N₂. Desorption at 850°C in N₂.

For further cyclic performance studies the 0.5wt.%, and the 1% Zr sample were tested in the fixed bed reactor at so short CO₂ uptake times that the conversion was below 10%, which is somewhat different from the relative long TGA adsorption times. These experiments should be closer to industrial conditions as e.g the initial CaL article from Shimizu et al. evaluated the CaL process using only 10% sorption capacity [3].

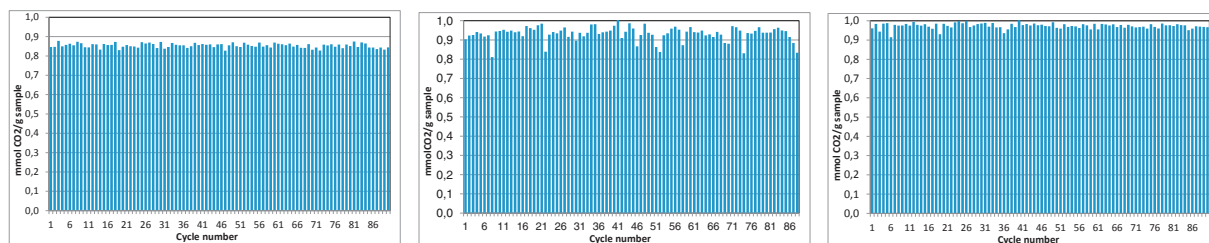


Figure 9. Left: Fixed bed data for calcined dolomite (the same data as shown in figure 4 right but included here for better comparisons with the Zr materials), 0.5wt.% Zr (middle), and the 1% Zr modified calcined dolomite (right). Adsorption at 600°C using 10% CO₂, 1% H₂O balanced in N₂. 10 minutes adsorption time for each of the 90 cycles. Desorption at 850°C using N₂. The conversion of calcined dolomite is quite stable at around 6.7% while the 1% modified sample was around 7.7%. The 0.5% Zr sample appears to be between these two materials if the somewhat unstable capacity from cycle to cycle is averaged.

As can be seen from the fixed bed reactor data there is a transition from the calcined dolomite, through the 0.5wt.% Zr sample to the 1wt.% sample with a further loss in performance when testing the 5 and 10 wt.% Zr materials (not shown).

Unused 1wt.%Zr and the same material after usage in 90 short adsorption cycle were studied by *in-situ* XRD. The figure below shows these results.

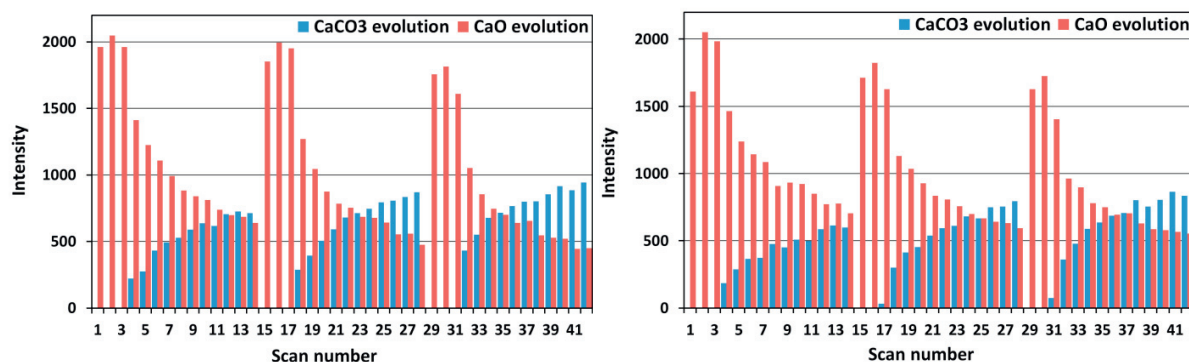


Figure 10. *in-situ* XRD plot showing the CaCO₃ and CaO evolution through 3 ad-des cycles. Left: Unused 1%Zr material. Right: 1%Zr after 90 cycles wet CO₂ in the fixed bed reactor. There are no big differences hence the material hasn't deactivated much during 90 cycles.

Comparisons of the *in-situ* XRD data for the 1wt.% Zr sample before and after 90 short adsorption cycles shows few, if any large changes. This is a strong indication that during use this material deactivates less compared to calcined dolomite even if it shows a higher working cyclic capacity.

t-resolved FTIR-spectra of calcined dolomite and the 1wt.% Zr sample at 600 °C exposed to a flow of 10% CO₂ in N₂ saturated with H₂O are shown in Fig. 11 below. Calcined dolomite is at the top and the Zr sample is at the bottom. As seen from the figure, the spectra were clearly different, and this difference suggests that the impregnation of 1 wt. % Zr alters the surface chemistry of the calcined dolomite.

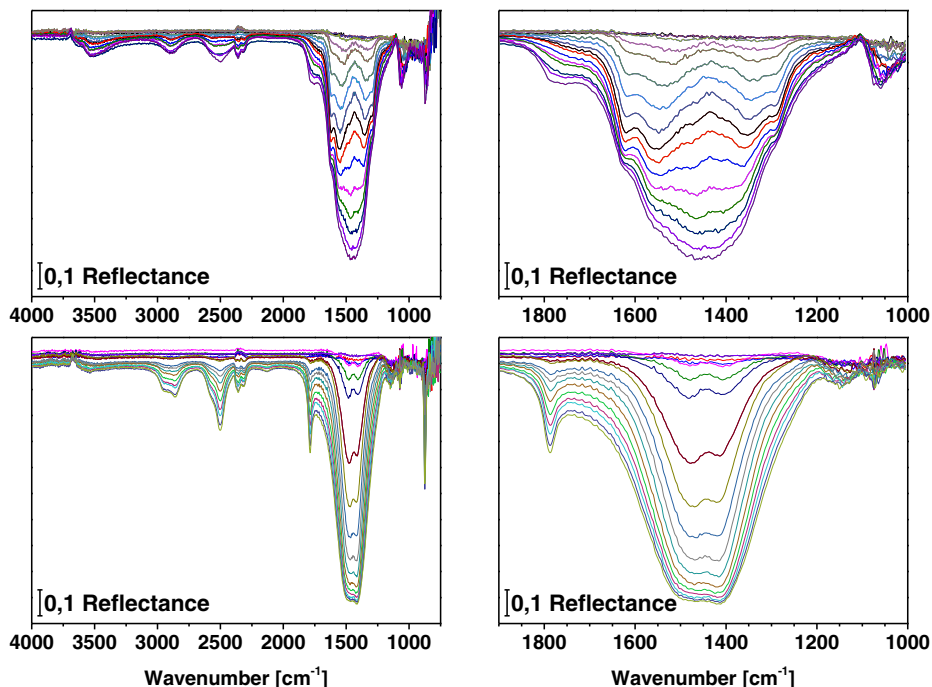


Figure 11. *t*-resolved FTIR-spectra collected during exposure to 10% CO₂ in N₂ bubbled through H₂O to calcined dolomite (upper) and 1 wt% Zr impregnated on calcined dolomite (lower). The spectra on the right hand side show the details for the region 1900 – 1000 cm⁻¹.

The region 1900 – 1000 cm⁻¹ is particularly revealing (enlarged at the right in figure 11). Calcined dolomite showed several bands; particularly at 1784, 1617, 1546, 1440, 1352, 1293, and 1066 cm⁻¹. Furthermore, their development with time was different. As seen, the bands that initially were the most dominant became less dominant with time. Finally, they appeared as mere shoulders on the dominant band centered at 1440cm⁻¹. The same observation was not made for the sample containing 1wt% Zr impregnated on calcined dolomite. As seen, there were three distinguishable bands centered at 1784, 1477, and 1413 cm⁻¹ at all times.

Although a full in-depth assignment of the bands is beyond the scope of this work, some tentative and general comments are warranted. First of all, we note that the number of bands observed for the sample impregnated with Zr shows the fewest number of bands, and we interpret this as a lower number of carbonate adsorption modes. It may be speculated that this is due to the formation of a Zr-containing surface layer that is less CO₂-reactive than the surface in calcined dolomite, and this interpretation would be in line with a perovskite layer as detected by PXRD. The band centered at 1784 cm⁻¹ is the only one in common for the two solids, and it may be assigned to bridging bidentate carbonate [18]. Both spectra also show bands that may be tentatively assigned to monodentate carbonate [19]. We also note a band that grows slightly upwards at 3691, and 3674 cm⁻¹ for the calcined dolomite and the 1 wt% Zr sample, respectively. This indicates that CO₂ may interact with some residual surface OH-groups after calcination, and that these OH-groups are different for the samples.

4. Conclusion

In this article we have described cyclic performance and deactivation trends of calcined dolomite and Zr modifications of the material in CO₂ sorption reactions. We found that above a certain level of Zr (more than 5wt.%) the surface and pores are likely blocked and the performance found inadequate. However, by using either 0.5wt% or 1wt.% Zr the BET surface are mostly still intact and the pore volume is only reduced by a factor of two. It is noteworthy that the 1% Zr sample showed a stable performance but with a lower total capacity compared to calcined dolomite in the TG apparatus but in the fixed bed reactor using short adsorption times the conversion was actually

better. The relative improvement was 15% and indicates that impregnating calcined dolomite, or maybe CaO, with small amounts of Zr may lead to very interesting cyclic performance properties at short adsorption times (which is more relevant from an industrial application point of view). However, Zr impregnated sorbents might not be used if e.g. CaL is used in conjunction with cement production since the spent sorbent is then used directly into the actual cement manufacturing so the Zr-modified sorbents might therefore be more suited in e.g. SE-SMR or CaL in conjunction with power production. Both the *in-situ* techniques (XRD and FTIR) applied in this work showed great potential for further fundamental studies.

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