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Studies of Ca-based high temperature sorbents for CO_2 capture

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Abstract

The natural mineral dolomite has been calcined and impregnated with Ti-, Zr-, Al-nanoparticle suspensions with the aim of improving the cyclic stabilities in high temperature CO_2 sorption processes. After impregnation and subsequent calcination the materials were characterized by N_2 adsorption (BET surface area and micropore volume) and powder X-Ray diffraction while the cyclic performance in CO_2 sorption processes was evaluated by breakthrough measurements: 30 cycles with sorption in 10% dry CO_2 at 600 °C and regeneration at 850 °C in N_2 were run on each sample.

Keywords: CaO; dolomite, sorbents; breakthrough experiments;

1. Introduction

Increasing political incentives on reducing anthropogenic greenhouse gases necessitates search for new technical solutions for controlling emissions from the diverse chemical- and energy industry worldwide. Large technological development efforts have been aimed towards utilizing energy and chemical production from renewables, however, it is consensus that on the short, and mid-term time horizon fossil fuels will be important and will be exploited for chemical and electricity production. A reduction of CO_2 emissions from (large) point sources is therefore crucial until more sustainable energy and chemical production process are in place. One main source of CO_2 emissions is power production, and for these sources there are huge efforts to enable large scale solvent based retrofit CO_2 capture units. These will likely be based on amines [1]. However, there are also other technological solutions that are based on the applications of membranes or sorbents that have potential uses. These technologies are at present less

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mature than solvent based processes but they represent important solutions for some applications within chemical and electricity productions.

In the present work solid sorbents applicable for high temperature processes will be presented and discussed. With high temperature it is implied sorbents operating at around 500-600 °C for sorption and 800-900 °C for regeneration (hydrotalcites are therefore excluded). There are currently two processes that are particular suited for sorbents working at these high temperatures, these two processes are the so-called "carbonate looping" and the sorption enhanced steam methane reforming (SE-SMR) [2,3]. In the carbonate looping process the CO_2 acceptors are used in a dual fluidized bed reactor in order to capture the CO_2 from the flue gases of coal or natural gas fired power plants. Hence this process is a variant of a post-combustion capture. In contrast the SE-SMR process is a process for hydrogen production with simultaneous CO_2 capture. The hydrogen, which has a purity of about 97-98 % if CaO is the active component, may then be further purified for the hydrogen market or burned for electricity generation. As in all processes that utilize powders decay/deactivation in some way is inevitable. Among others high reaction rates and large sorption-capacity vs. lifetime are important. As a consequence of the somewhat limited performance of easily accessible natural minerals such as lime and dolomite, a lot of research has been aimed towards making new artificial (nano)materials. However, due to CaO's favorable thermodynamic properties combined with relatively fast reaction rates a lot of research has focused on making materials that have CaO as the active phase, possibly fixed in a suitable matrix. Among modified CaO materials some examples are: Thermal pre-treatments of lime [4], hydration of lime [5], doping CaO by $KMnO_4$ [6], dispersion of CaO on various supports like e.g. $Ca_{12}Al_{14}O_{33}$ or $CaTiO_3$ [7, 8], or co-precipitation of Ca with other elements (M) like Cr, Mn, Co, Cu, or Ce, for a nominal composition of $Ca_{0.9}M_{0.1}O_x$ [9], or CaO on MgO mixed with $Ca_9Al_6O_{18}$ [10], or CaCeZrOx [11].

Actually, one of the main motivations for the present study was that very stable multi-cycle performance could be obtained in mixed nano-crystals of synthetic CaCeZrOx [11]. We therefore wondered if also addition of nano-particular oxides of specific element could have a stabilizing effect on natural calcium containing sorbents such as calcined dolomite. In this work we present our initial work along this line where our goal is to stabilize the natural mineral dolomite in order to improve it's lifetime as a CO_2 sorbent for high temperature applications. The dolomite mineral used is from Seljelid in Norway and various materials have been made by impregnating the calcined dolomite with aqueous dispersions of Al, Zr or Ti nano-particles. These materials have been studied by among others with XRD and breakthrough measurements and compared to the reference material (calcined dolomite)

2. Experimental

In the following subsections the various material characterization techniques are presented. The data and discussion of these are in section 3.

The starting material in this work is the natural mineral dolomite ($CaMg(CO_3)_2$) from Seljelid, Norway. In order to prepare dolomite as an acceptor for CO_2 the oxide version was formed by heat treatment (calcination) of the mineral for 12 hours at 900°C in 10% H_2. This procedure transformed the dolomite into an oxide form that can be termed CaOMgO (there is close to a 1:1 ratio of Mg and Ca). Furthermore, a reference material (sample A) was made by another heat treatment in air at 1000°C for 15 hours in order to be comparable to the surface modified versions of it, *vide infra*. Three other samples, termed B, C, and D, was made by depositing sample A with Ti-, Zr-, and Al- nanoparticles with a subsequent calcination. The nano-particles were all in aqueous solutions and deposition were done using the incipient wetness technique. The solutions (all from Aldrich) were: Zirconium (IV) oxide nanoparticles, dispersion, <100nm (BET), 10wt.% in water; Titanium (IV) oxide, dispersion, mixture of rutile and anatase, <150nm, 33-37wt.% in water; and Aluminum oxide, dispersion, <50nm (TEM),

20wt.% in water. Sample B, C, and D all have a nominal 10wt.% content of either Ti, Zr, or Al. After impregnation the samples were calcined in air for 15 hours at 1000°C.

N_2 BET surface and micorpore volume were measured on all samples. These data are reported in Table 1 in section 3.

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 CuK$_{\alpha1}$ radiation (λ= 1.54060 Å) and a step size of 0.013 degrees.

In order to asses the CO_2 uptake/desorption capacity and kinetics, we tested the materials in a breakthrough apparatus. Figure 1 below shows schematically the principle of the test rig and a typical raw data output.
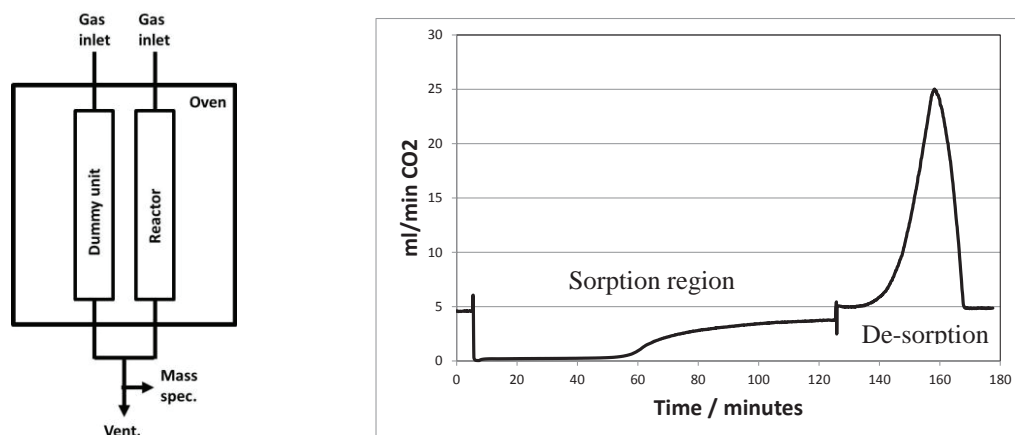

Figure 1. Left: Principle of the breakthrough rig and example of breakthrough curve. Right: The black line is the MS CO_2 signal (actually the m/z=44 signal)

The inner diameter of the reactor tubes where 1 cm and we applied a 4 cm high bed. The amount sorbent was typically between 2.5 and 3 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 flow was pure N_2 and the other was 9.15% CO_2 balanced in N_2. The CO_2 flow was therefore about 4.6 ml/min at room temperature. 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 30 cycle test the reactor tubes were heated to 600 °C by an electrically furnace. Pure N_2 was entering the reactor with the sorbent while the CO_2 containing gas entered the dummy reactor. At this stage the continuous CO_2 MS signal (m/z = 44) shows the intensity of 4.6 ml/min CO_2 (the first minutes of the MS trace below). After ten minutes at 600 °C a valve switched so that CO_2 gas enters the reactor tube with sorbent and the pure N_2 gas enters the dummy reactor. The valve switch is seen by a spike after ca. 5 minutes. During sorption CO_2 is reacting with the sorbent and is removed from the gas phase and the MS signal from CO_2 declines. When CO_2 is reacting with CaO $CaCO_3$ is formed. At our applied conditions CO_2 does not react with MgO. The initial sorption is shown in figure 1 from about 5-7 minutes. After some time the CO_2 MS signal starts to increase indicating a breakthrough, i.e. the sorbent does not absorb all the CO_2 entering the bed. Further on the MS signal from CO_2 rises almost to the initial level before sorption took place. After 120 minutes with CO_2 gas over the sorbent the gases are switched again and the temperature was increased to 850 °C. As one can see the sorbent is not fully loaded with CO_2 at our applied conditions since the CO_2 level in the MS trace is still yet not back to the

original level it had before sorption. Other reaction conditions, like e.g. higher partial pressure of CO_2, added steam, or other temperatures will changes this picture but the general features of the curve would still be the same. During the heating period in N_2 (regeneration) the sorbent released the previously absorbed CO_2 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. A 30 cycle experiment lasted for about a week. The absorption capacity was in this work evaluated at 10% slip and the data are presented as mmol CO_2 pr. gram sorbent. 10% slip, i.e. when the MS signal indicated about 0.46 ml/min flow, is the opint where the MS signals start to rise, i.e. at appr. 55 minutes in the curve to the right in Figure 1.

3. Results and discussion

N_2 BET areas and micropore volumes of the samples were measured and reported in Table 1.

Table 1. Material summary

Sample ID	Type	BET area, m^2/g	Micropore volume, cm^3/g
A	Calcined dolomite	11,6	0,21
B	Ti modified	8,0	0,10
C	Zr modified	15,1	0,20
D	Al modified	12,8	0,16

The data shows that there are quite large relative differences; however, the magnitudes of the data are in the same order. Figure 2 shows a stacked plot of the XRD data of our materials. The main peaks are reflections form CaO and MgO phases but in samples B, C, and D there are additional peaks. The are indicates and listed in Table 2 below
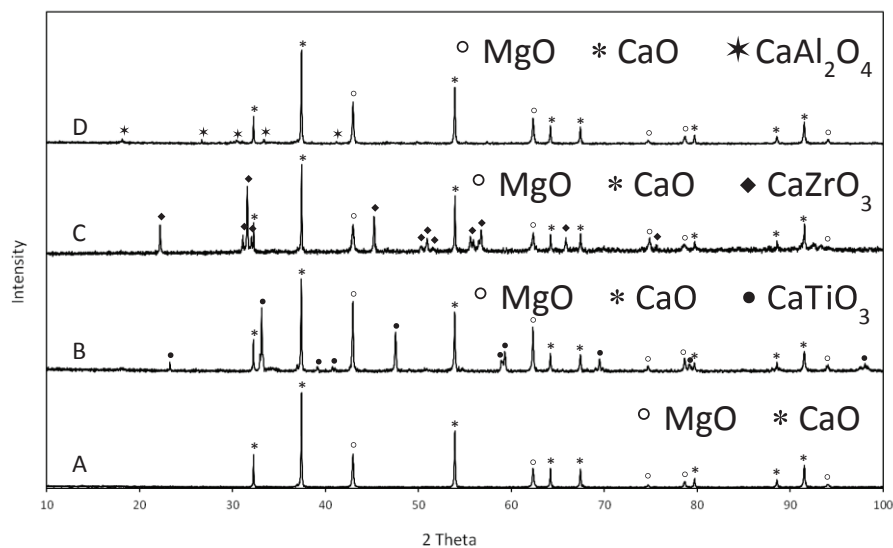

Figure 2. X-ray diffractograms of the samples. The main reflections are due to CaO and MgO phases but in samples B, C, and D there are additional reflections.

As one can assess form the XRD data the main phases are as expected CaO and MgO. However, it is observed that sample B and C have each an additional perovskite phase, $CaTiO_3$ and $CaZrO_3$, respectively, which are likely not active in the sorption process. Sample D has the additional phase $CaAl_2O_4$. This is a typical form that can be formed in Al oxides. For samples B, C, and D it appears that all the added metal (Ti, Zr, and Al) is completely transformed into a Ca-metal-oxide since the XRD data are fitted very well to the abovementioned phases. As a consequence the specific sorption capacity must be lower compared to sample A due to less active components, i.e. CaO. By simple stoichiometric calculations one may estimate the loss of Ca from the active CaO part into the inactive phases. The relative mole loss of CaO in percent relative to sample A is reported in Table 2.

Table 2. XRD summary

Sample ID	Type	Main phases	Additional phases	Percent moles CaO loss relative to sample A
A	Cal. dolomite	CaO, MgO	-	-
B	Ti modified	CaO, MgO	$CaTiO_3$	22%
C	Zr modified	CaO, MgO	$CaZrO_3$	12%
D	Al modified	CaO, MgO	$CaAl_2O_4$	20%

The breakthrough data analyses for the samples are shown in Figure 3 below. These data show the CO_2 uptake capacity in mmol/gr sorbent plotted against cycles (defined above and there is 30 in total for each experiment).
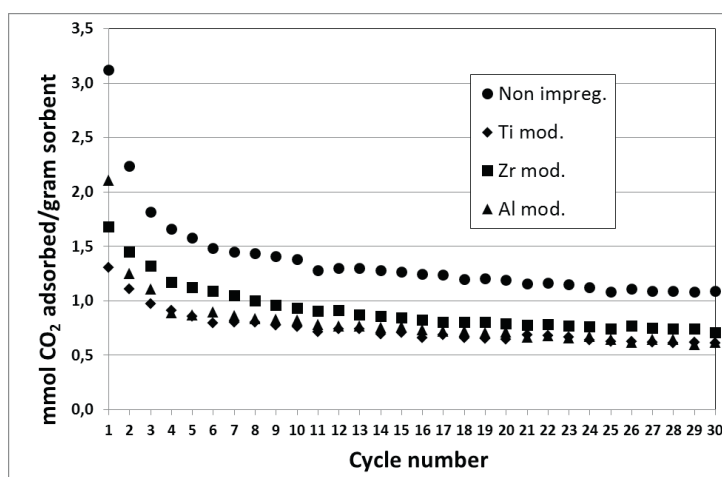

Figure 3. Breakthrough data. The amount CO_2 adsorbed was evaluated at 10% slip. The plot is mmol CO_2 pr gram sorbent versus cycle number.

The typical decline after the first sorption cycle is evident for all four samples. This effect is common for all natural sorbents and typical for many artificially made sorbents. Note that the full CO_2 capacity for calcined dolomite (CaOMgO) is around 10 mmol/gram.

Sample A shows the highest uptake before breakthrough with approximately 3.1 mmol/gram absorbed CO_2. Sample D (Al modified) shows the second largest uptake for the first cycle, about 2.2 while the two other samples (B and C) shows about 1.4 and 1.7 mmol/gram sorbent, respectively. All samples have

declining capacity but sample B-D shows the least initial degradation. One explanation for the lower capacity for samples B, C, and D is that some Ca is fixed in new phases, but that not explains the whole loss so there must also be some pore/surface blocking also.

It is known that performance loss of CaO sorbents may be due to physical degradation of the particles induced by cracks etc. The present work has so far not yet been able to assess whether the dominating deactivation seen is due to sintering or physical degradations, or both. Further studies must be aimed towards these issues. However, Figure 3 indicates that surface modifications of calcined dolomite may give a more stable material when it comes to cyclic performance. In addition, the CO_2 sorption kinetics of the presented materials are still good and it is known that the actual applied capacity during operating could only be a small part (~5-10%) of the total capacity as described in our recent work on the use of calcined dolomite in the SE-SMR process and using a circulating fluidized bed reactor [12].

As indicated above, an interesting feature with breakthrough experiments is the possibility of evaluation of the sorption and desorption kinetics. In our system there is no bypass of gases in the reactor and the relatively high powder bed, combined with low gas flow, ensures that the curve shapes should give quite reliable information on sorption-desorption kinetics. Figure 4 below shows the first 100 minutes of sorption of three first sorption curves for sample A.
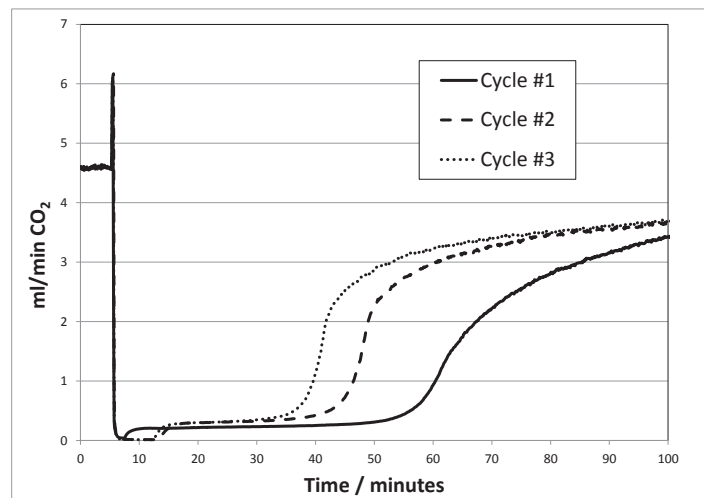

Figure 4. About 95 minutes of the three first breakthrough curves for sample A as measured by the online continuous MS.

As one can see the initial sorption is similar and fast for the cycles as can be seen by the rapidly declining CO_2 signal. However, after a short time there is a tiny breakthrough before the curve are somewhat flat for 30-50 minutes when they start to rise towards 3.5 ml/min CO_2 flow at about 100 minutes. After that a slow rise towards a full loaded material is seen. It is therefore three regions and the observed effects can be justified with a kind of core-shell model for the sorption. Except for the first cycles, which is somewhat varying in shape from sample to sample, cycle 2 and 3 shown here are similar in shape to all other cycles in all other samples. In experiments not shown here, the first cycle could have a almost completely flat curve until breakthrough started at 50-60 minutes, but from the second cycle all

cycles show the same behavior as the curves shown in Fig. 4. We have yet no detailed model describing these curve shapes but our data could indicate that there is an initially layer that hinders the sorption a little, but not until after about 50 minutes (first cycle) the curve rises much more and we have likely formed a large carbonate layer that gives resistance to further sorption. Subsequent sorption is dependent upon the relatively slow diffusion of CO_2/CO_3^{2-} towards the inner parts of the various crystallites. The fact that we observe two steps where sorption is reduced indicates that there could initially be sorption on very easily accessibly CaO sites while shortly after a sort of small resistance towards sorption has formed.

4. Conclusion

Calcined dolomite and three different surface modified versions of it have been tested as high temperature CO_2 sorbents for possible high temperature applications processes like e.g. sorption enhanced steam methane reforming or the carbonate looping process. The materials are impregnated with Ti-, Zr-, and Al nanoparticles with a subsequent calcination, and they are characterized by surface and pore volume measurements and powder XRD. The XRD data show that in addition to CaO and MgO $CaTiO_3$, $CaZrO_3$, and $CaAl_2O_4$ are formed in respective synthesis. Breakthrough measurements show that the surface modified materials have less capacity (measured at 10% slip) compared to the calcined dolomite. However, the cyclic stability is ok and the surface modification principle is likely to have some potential of improving natural sorbents.

Acknowledgments

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