Novel Carbon Dioxide Solid Acceptors Using Sodium Containing Oxides

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ABSTRACT

The use of solid acceptors for CO_2 sequestration has been widely used in many new applications. Recent developments in the field are based in the use of synthetic CO_2 acceptors for high-temperature applications (400–700°C), which include compounds such as lithium zirconate (Li_2ZrO_3) and lithium orthosilicate (Li_4SiO_4). Sodium-based oxides have been used in the past either as low-temperature (<250°C) CO_2 acceptors or as promoters for lithium-based acceptors. In this study we report the use of Na-based acceptors at high temperatures as an alternative for lithium based CO_2 acceptors with the use of thermogravimetric (TGA), and X-ray diffraction (XRD) analysis. Na-based acceptors were prepared by the solid-state method, and the sorption/desorption property was examined by TGA. In the first part of the study sodium acceptors

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prepared included: Sodium titanate (Na_2TiO_3), sodium antimoniate (Na_3SbO_4), and sodium zirconate (Na_2ZrO_3). TGA experiments at 600°C showed Na_2ZrO_3 to have the highest activity toward CO_2 sorption, followed by Na_3SbO_4 and Na_2TiO_3. In the second part of the study Li_2ZrO_3 and Li_4SiO_4 were prepared by the solid-state method for comparison purposes. Na_2ZrO_3 TGA data showed the highest sorption rate at 600°C compared to Li_4SiO_4 and Li_2ZrO_3. However, regeneration performance was not as good as Li_4SiO_4 and Li_2ZrO_3. In a two-cycle run Na_2ZrO_3 presented good sorption and regeneration performance. Experimental data showed that Na-based sorbents can be used as an alternative for solid CO_2 acceptors at high temperatures and particularly Na_2ZrO_3 is a candidate to compete with current synthetic sorbents such as Li_4SiO_4 and Li_2ZrO_3 when costs of materials are involved.

Key Words: CO_2 sorbent; High temperature CO_2 sequestrian; $NaZrO_3$; Na-based CO_2 absorbent.

INTRODUCTION

World economy in the present relies on burning fossil fuels to produce affordable energy. A consequence of the use of these fuels is the emission of important quantities of carbon dioxide (CO_2) to the atmosphere creating environmental problems such as global climate warming. In the near future Industry, if mandated to remove CO_2, will certainly require improved and novel technologies for the efficient removal of CO_2. Therefore, there is a need to develop alternate processes that may improve energy savings and conversion efficiencies in the energy generation combined with reduction of CO_2 emissions to the atmosphere. Among such technologies is the use of the CO_2 sequestration concept that in many cases has proven to be an alternative.[1] Examples of such processes are the CO_2 capture during coal gasification,[2] the sorption enhanced reaction (SER) for the production of hydrogen,[3] and the use of inorganic membranes for CO_2 separation in the molten carbonate fuel cells (MCFC).[4]

The use of solid acceptors for CO_2 sequestration have been widely used in the past and started several years ago for the CO_2 separation in the coal gasification process.[5] Several investigators examined the effects of temperature, pressure, and reactive gas composition of calcium oxide (CaO) based materials using thermo-gravimetric (TGA) reactor techniques.[6,7] However, degradation of these materials was observed during multicycle tests. Calcined dolomite (a natural mineral containing mainly calcium and magnesium carbonates) proved to be superior in multicycle performance to previous CaO based past materials.[6] However, high regeneration temperatures were needed (950°C) using this acceptor of mineral nature. Also of mineral

nature hidrotalcites ($Mg_6Al_2(CO_3)(OH)_{16} \cdot 4H_2O$) were used by Hufton et al.[8] and Ding and Alpay,[9] at relatively high temperatures 400–550°C. However the sorption capacity of these hidrotalcites were low.

Recently, Ohashi et al.[10] developed a novel synthetic CO_2 separation technique by using lithium zirconate (Li_2ZrO_3) as a solid CO_2 acceptor in the temperature range of 450–700°C. However, the reaction sorption rate was very slow. Other proposed acceptors based on lithium were lithium ferrite ($LiFeO_2$), lithium nickel ($LiNiO_2$), lithium titanate (Li_2TiO_3), lithium methasilicate (Li_2SiO_3) and lithium orthosilicate (Li_4SiO_4) used at various temperatures.[11] Certainly, among all these Li_4SiO_4 was found to have the highest capacity and reactivity with CO_2.[12]

It was also reported that potassium carbonate dispersed on Li_2ZrO_3 added as a promoter increased the sorption rate compared to Li_2ZrO_3 alone.[13] Ichi Ida and Lin[14] and Ohashi et al.[15] explained with the use of a reaction model TGA-DSC data how such carbonates formed an eutectic mixture of lithium carbonate and potassium carbonate (Li_2CO_3-K_2CO_3) that helped to improve Li_2ZrO_3 sorption kinetics.

Ohashi et al.[10] also used other alkali carbonates as promoters for Li_2ZrO_3 sorption kinetics. Examples of such promoters used by Ohashi et al. were sodium carbonate (Na_2CO_3), potassium carbonate (K_2CO_3), magnesium carbonate ($MgCO_3$) and calcium carbonate ($CaCO_3$). However, sodium oxides by themselves have not been reported to have a significant high-temperature performance (greater than 400°C). Sodium carbonates and oxides were only reported to show promoting effects on Li_2ZrO_3 and Li_4SiO_4 added in a maximum amount of 30% mol.[11] This paper reports the use of novel CO_2 acceptors using sodium-containing oxides in the temperature range of 600–700°C. The oxides described here react reversibly with CO_2 through the following reaction:

$$Na_2MeO_3 + CO_2 \Longleftrightarrow Na_2CO_3 + MeO_2 \tag{1}$$

Where Na_2MeO_3 represents a sodium mixed oxide such as sodium antimoniate (Na_3SbO_4), sodium titanate (Na_2TiO_3), and sodium zirconate (Na_2ZrO_3). In this study we examine the CO_2 sorption and desorption characteristics of these oxides with the help of thermogravimetric analysis (TGA), X-ray diffraction (XRD), particle size, and density.

EXPERIMENTAL SECTION

Figure 1 shows the experimental procedure followed in the present work. First, the acceptors were prepared through the solid-state method (mixing) described below and calcined to the required temperature. Next, the generated

Experimental Procedure

Figure 1. Experimental procedure followed in the present work.

samples were characterized by X-ray diffraction (XRD), particle size and density determination. Finally, the CO_2 sorption/regeneration performance of each sample was evaluated through thermogravimetric measurements (TGA).

Synthesis and Characterization of Na-Oxides

Na_2ZrO_3, Na_2TiO_3, and Na_3SbO_4 were prepared by the solid-state method. Lithium zirconate (Li_2ZrO_3-F14) and lithium orthosilicate

(Li$_4$SiO$_4$-F56) were also prepared for comparison purposes. Starting materials were reagent grades from Sigma-Aldrich and details of preparation conditions are summarized in Table 1. Most of the precursors used were oxides combined with carbonates, with the exception of zirconium and lithium materials, which used zirconium acetylacetonate and lithium acetate, respectively. Preparation was preformed as follows: the precursors were weighted, grounded, and intimately mixed in an agate mortar. Most of the precursors were mixed in a 1 : 1 molar ratio, except for sample Na$_2$ZrO$_3$-F61 that used a 10% excess of sodium carbonate. The mixtures were calcined at temperatures reported in Table 1 for 4h using alumina crucibles in an atmospheric air-heated furnace. Although, the same preparation procedure was used for all the samples, different calcination temperatures were employed. These temperatures were determined through thermodynamic analysis of the desired final crystal phase. The final average particle size in microns (μm) of each sample was measured with a laser-counting Mastersize 2000 (Malvern Instruments) and is reported in Table 1 with all of the samples being less than 10 μm. Density of the calcined samples was measured with the use of an ultra-pycnometer 1000 (Quantachome Instruments) and all samples showed an average density of 4.0 g/cm^3 with the exception of Li$_4$SiO$_4$ (F66), which had a lower density of 2.2 g/cm^3.

Figure 2 shows the XRD patterns of the synthesized acceptors: Na$_2$ZrO$_3$-F34A, Na$_2$ZrO$_3$-F61, Li$_2$ZrO$_3$-F14, and Li$_4$SiO$_4$-F66. Most of the XRD patterns in Fig. 2 show pure phases after calcination. Na$_2$ZrO$_3$-F34A pattern shows some unreacted ZrO$_2$ peaks still present in the sample. Preparing Na$_2$ZrO$_3$-F61 at the higher calcination temperature of 900°C and using 10% excess sodium eliminated this impurity. After that the XRD pattern of the Na$_2$ZrO$_3$-F61 showed no impurities at all. Also some small peaks corresponding to ZrO$_2$ were found in sample Li$_2$ZrO$_3$-F14. However, the

Table 1. Synthesized sorbents prepared by solid state method.

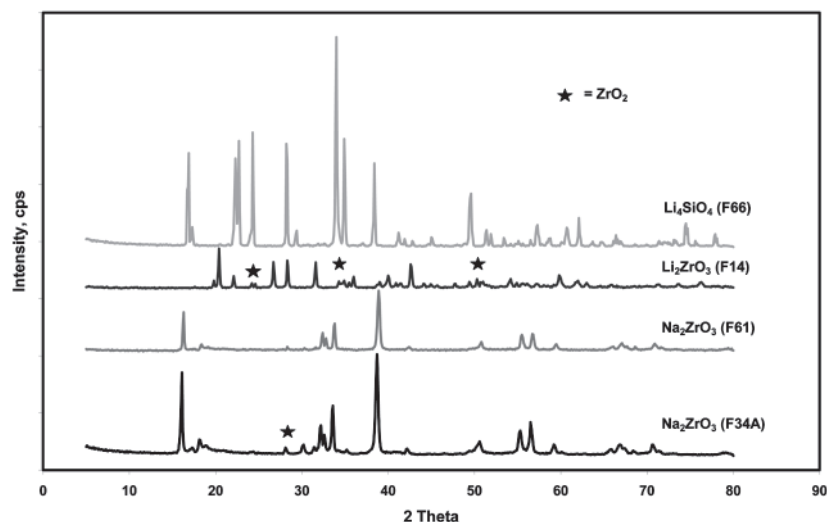| Sample	Precursors	Molar ratio	Calcination temperature	Density g/cm^3	Average particle size μm
Na$_2$TiO$_3$-F41	TiO$_2$: Na$_2$CO$_3$	1 : 1	700°C	3.14	3.22
Na$_3$SbO$_4$-F54	Sb$_2$O$_3$: Na$_2$CO$_3$	1 : 1	950°C	4.15	4.23
Na$_2$ZrO$_3$-F34A	Ac Ac Zr : Na$_2$CO$_3$	1 : 1	800°C	4.25	7.84
Na$_2$ZrO$_3$-F61	Ac Ac Zr : Na$_2$CO$_3$	1 : 1.1	900°C	4.74	5.25
Li$_2$ZrO$_3$-F14	Ac Ac Zr : Li$_2$CO$_3$	1 : 1	950°C	3.87	4.62
Li$_4$SiO$_4$-F66	SiO$_2$: LiOOCCH$_3$	1 : 1	950°C	2.22	8.36

Ac Ac Zr = Zr[CH$_3$COCO=C(O)CH$_3$]$_4$.

Figure 2. XRD patterns of synthesized Na-based oxides.

presence of small quantities of ZrO_2 in Li_2ZrO_3 is believed to not influence the sorption performance of this sample.[10]

Figure 3 shows the XRD patterns of samples Na_2TiO_3-F41 and Na_3SbO_4-F54, respectively. Here, in the case of sample F54 the crystal phase of Na_3SbO_4 is mixed with $NaSbO_3$ and in the case of sample F41 is mixed with Na_xTiO_4. A higher calcination temperature (900°C) was tried to get rid of the unwanted crystal phases. However, poor-reactive high molecular weight titanates such as $Na_8Ti_5O_{14}$ were produced.

RESULTS AND DISCUSSION

CO_2 Sorption and Desorption of Na-Based Oxides

About 20–30 mg of the synthesized oxides were placed in a sample pan of a TGA microbalance system Pyris 1 (Perkin Elmer) to be tested for their CO_2 sorption-desorption performance. Passing UHP argon during heating up to the reaction temperature of 600°C for about 40 min dried the samples. Then, the CO_2 sorption reaction started by admitting a flow of 150 mL/min of 100% CO_2. After sorption was completed, the samples were heated to their corresponding regeneration temperature. During regeneration 850°C
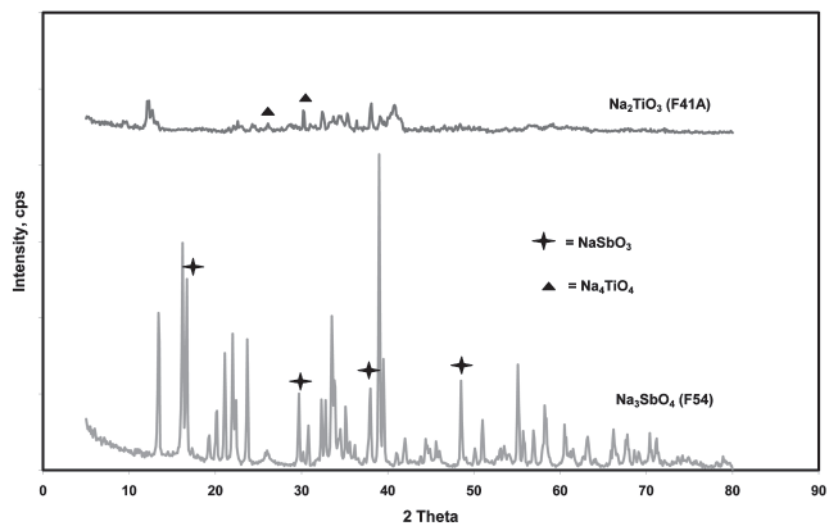
Figure 3. XRD patterns of samples F41A and F54.

was used for Na_3SbO_4-F54, 780°C for Na_2ZrO_3-F34A and Na_2ZrO_3-F61, and 700°C for Na_2TiO_3-F41. After reaching the appropriate temperature, 100% air was admitted to the TGA for the regeneration to proceed. Finally, after regeneration was completed, the sample was rapidly quenched to room temperature for further characterization. Details of sorption and regeneration performance of each acceptor are shown in Table 2.

Figure 4 shows the CO_2 sorption TGA response of the Na-based sorbents. Sample Na_2TiO_3-F41 presented the lowest sorption with only 8% weight

Table 2. Sorption/regeneration performance of synthesized CO_2 acceptors.

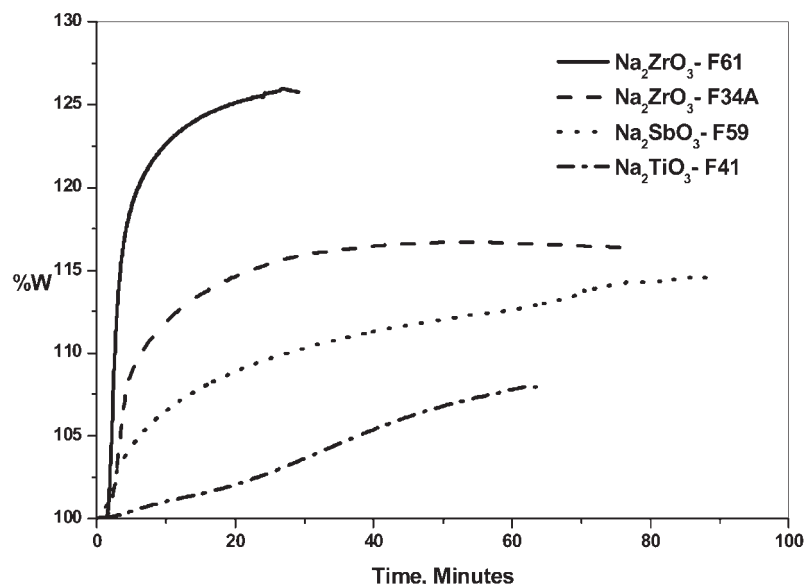| Sorbent	T Reg. (°C)	Sorption rate (%W/min)	Regeneration rate (%W/min)	CO_2 absorbed (%)	CO_2 released (%)	Max. theoretical sorption (%)
Li_2ZrO_3-F14	780	0.0318	5.55	13.07	11.67	28.7
Na_2TiO_3-F41	700	0.1097	0.043	8	10	26
Li_4SiO_4-F66	700/780	1.15	7.5	30	29	36.7
Na_3SbO_4-F54	850	2.47	2.01	14.5	14.5	20.4
Na_2ZrO_3-F34A	780	3.34	0.531	16.68	11.5	23.7
Na_2ZrO_3-F61	780	10.33	1.02	25.77	22	23.7

Figure 4. TGA response of synthesized Na-based CO_2 acceptors.

change. Also the initial global rate was the slowest among all the sodium-based sorbents with 0.1097 %W/min. The particular low sorption value observed with this sorbent can be attributed to the presence of other high molecular titanates produced at temperatures $>700°C$ that were found to be less reactive to CO_2 such as the one observed in the XDR pattern of Fig. 3. Sample Na_3SbO_4-F54 resulted in the next higher sorption rate with 0.1097 %W/min and a sorption of 14.5 %W, which is about 70% of its maximum theoretical sorption of 20.4%. This sorbent has the opportunity to be further improved through optimization of its synthesis parameters to produce a purer Na_3SbO_4 phase. Also in Fig. 4 can be observed that compounds containing Na_2ZrO_3 were the ones that produced faster sorption rates and higher CO_2 sorption. According to the results of Table 2 sorbent Na_2ZrO_3-F34A had an initial sorption rate of 3.34 %W/min and showed a CO_2 sorption of 16.68% which is about 70% of its theoretical maximum. With this promising results it was decided to further improve sample F34A to get rid of the unreacted ZrO_2 present in the XRD pattern. Therefore, sorbent Na_2ZrO_3-F61 was prepared using excess Na of 10% molar basis combined with smaller particle size and higher calcination temperature. These modifications resulted in the sorption TGA response observed in Fig. 4. Sorbent Na_2ZrO_3-F61 not only showed an improved sorption rate value of 10.33 %W/min (about three times higher than F34A), but in an increased

sorption capacity of 25% which is 2% higher than the theoretical maximum. This last behavior can be attributed to the excess of Na present originally in the sorbent after calcination that reacted towards Na_2CO_3.

Comparison of Na_2ZrO_3 with Current Synthetic CO_2 Solid Acceptors

Current solid CO_2 acceptors reported in literature lately are: Li_4SiO_4 and Li_2ZrO_3. Masahiro et al.[11] reported a modified lithium silicate (Li_4SiO_4), which consisted on Li_4SiO_4 promoted with potassium carbonate (K_2CO_3) to form an eutectic solution at high temperatures accelerating the sorption rate of this sorbent. In a TGA test this modified Li_4SiO_4 absorbed 27%W in 50 min at 500°C and 20% CO_2. Masahiro et al. also compared this sorbent with modified-Li_2ZrO_3 to show the superior sorption performance of lithium silicate. In their tests modified Li_2ZrO_3 only absorbed 17%W in 50 min. We also ran our Na_2ZrO_3-F61 at the same conditions used by Masahiro et al. (500°C, 20% CO_2) and it performed in between Li_4SiO_4 and Li_2ZrO_3 with a sorption of 20.71%W in 50 min (not shown in Fig. 4) with a sorption rate also in between the two previously reported sorbents. It is important to mention that our sorbent Na_2ZrO_3-F61 was not modified with the addition of a promoter for this test.

In order to better compare these sorbents Li_4SiO_4-F66 and Li_2ZrO_3-F14 (without promoter) were prepared at out laboratory and their synthesis details and some properties are described in Table 1. Also it was decided to compare these sorbents with our best Na-based sorbent Na_2ZrO_3-F61. TGA tests were performed at 600°C and 100% CO_2 (as described previously) and comparison of these tests are presented in Fig. 5. From Fig. 5 it can be seen that the highest sorption was achieved by Li_4SiO_4-F66 with about 30%W, in good agreement with Masahiro et al.[12] data, followed by our Na_2ZrO_3-F61 with 25.77%W and finally Na_2ZrO_3-F34 and Li_2ZrO_3-F14 with 16.68%W and 13%W, respectively. However, sorption of Li_4SiO_4-F66 was completed after 30 min, while for Na_2ZrO_3-F61 took only 25 min. Table 2 also show the sorption rate as observed in theses tests. From these values and Fig. 5 it is evident that the order from higher to lower sorption rate is as follows: Na_2ZrO_3-F61 > Na_2ZrO_3-F34A > Li_4SiO_4-F66 > Li_2ZrO_3-F14. Therefore, the highest sorption rate was achieved by Na_2ZrO_3-F61, which was three times faster than Na_2ZrO_3-F34A and almost nine times faster than Li_4SiO_4-F66. Also it is evident the low performance of Li_2ZrO_3-F14 at these conditions. These previous results agreed with data reported by Masahiro et al.[12] in the fact that Li_4SiO_4 is superior in performance to Li_2ZrO_3 at the same conditions. However, it is surprising that Na_2ZrO_3 posses better rate sorption performance than Li_4SiO_4.
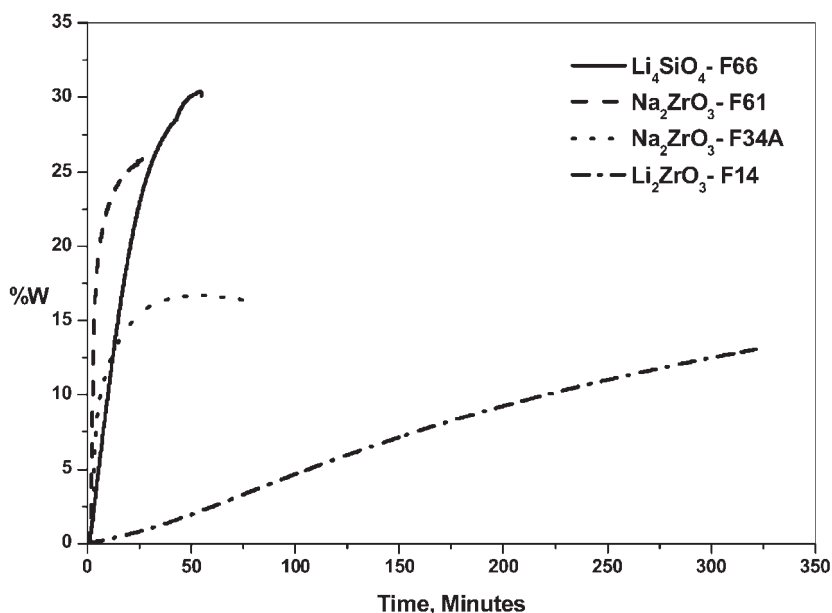
Figure 5. TGA response for sorbent comparison at 600°C, 100% CO_2.

Regeneration of the Synthesized Sorbents

A very important feature of these sorbent materials is that they have to be regenerated to be used for many cycles in a continuous fashion. Table 2 also shows the regeneration performance in a TGA of all the sorbents synthesized in our laboratory. Regeneration was performed under an atmosphere of 100% air at a flowrate of 150 mL/min. Regeneration rate from highest to lowest was as follows: Li_4SiO_4-F66 > Li_2ZrO_3-F14 > Na_3SbO_4-F54 > Na_2ZrO_3-F61 > Na_2ZrO_3-F34A > Na_2TiO_3-F41.

Li_4SiO_4-F66 presented the highest regeneration rate with 7.5%W/min at 700°C in its initial part followed by an increase in regeneration temperature at 780°C. Li_4SiO_4 was also regenerated with only 1%W less than the amount absorbed. The next better regeneration rate was observed for Li_2ZrO_3-F14 with only 1.4%W less than the amount absorbed. This was followed by Na_3SbO_4-F54, which released the same amount of CO_2 absorbed. Na_2ZrO_3 sorbents showed a slower regeneration rate compared to the sorbents described above. Also the amount of CO_2 released was slightly lower than the absorbed by these two samples. It is important to note here that the excess in Na present in the sample Na_2ZrO_3-F61 was not regenerated. This

may explain why the amount of CO_2 released (22%W) was much lower than the absorbed (25%W). This behavior is the most troubling for the Na_2ZrO_3 acceptor and it is yet to be studied in further experimental work, which may involve the addition of an eutectic mixture as a promoter of the reaction/ regeneration rate.[15] Finally Na_2TiO_3-F41 showed the lowest regeneration rate. The fact that the amount of CO_2 released was higher than the absorbed can be explained through the instability of the sample to form many different titanate phases at the regeneration temperature.

Cycles

For a continuous process to be possible it is needed for the sorbent to be stable through sorption and regeneration cycles. Figure 6 shows two sorption/ regeneration cycles of Na_2ZrO_3-F61. During the first cycle F61 absorbs 25.6%W at a temperature of 600°C. After the first sorption was completed temperature was raised to 660°C and finally to 780°C for the regeneration to proceed. After regeneration of the first cycle the weight change was 23.4%W, which is almost the same weight change that would experience
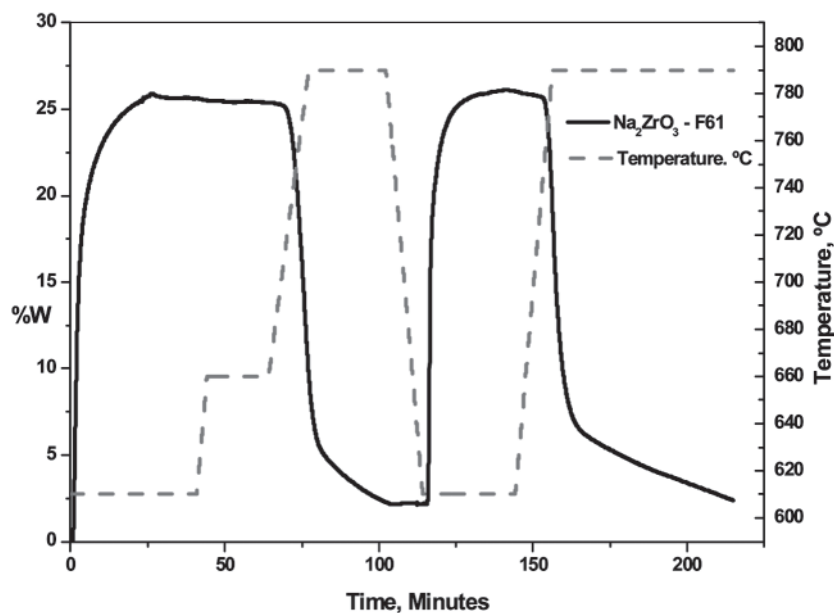

Figure 6. Two-cycle response of sample Na_2ZrO_3-F61.

pure Na_2ZrO_3, since the maximum theoretical is 23.7%W. It is possible to say that during regeneration the excess of Na remains in the sorbent in a carbonate form (Na_2CO_3) and without free ZrO_2, regeneration of this excess carbonate would not be possible, since regeneration of pure Na_2CO_3 would require temperatures as high as 2300°C. This behavior could explain the fact that a lower weight change during the first cycle was observed after regeneration. On the other hand, the weight change during sorption of the second cycle was 23.93%W, which compared to the regeneration weight change of 23.73%W was almost the same. The most troubling feature of the two-cycle performance of Na_2ZrO_3-F61 is the slow final rate observed during regeneration that is particularly slower in the case of the second cycle. This behavior was before observed during regeneration of sorbents F34A and F61. It is possible that diffusion of CO_2 through Na_2CO_3 present, as excess of Na in the final part of regeneration is responsible for such lower regeneration rate.

CONCLUSIONS

The use of solid Na-based oxides in former applications related to CO_2 sorption at high temperatures (T > 400°C) have been reported in literature only as promoters of Li_2ZrO_3 and Li_4SiO_4, but never as CO_2 sorbents as themselves.[10] The novelty of this research is based in the fact that Na-oxides are able to capture CO_2 at high temperatures (600°C), which make these kind of oxides particularly attractive for the sorption enhance reaction process for the production of hydrogen.[3]

As Na-based sorbents, the highest activity towards CO_2 sorption was presented by Na_2ZrO_3, followed by Na_3SbO_4 and finally by Na_2TiO_3.

The use of a 10% excess of sodium in Na_2ZrO_3 was responsible for the increase in purity, reactivity and sorption capacity compared to stoichiometric Na_2ZrO_3.

Na-based sorbents can be used as an alternative for solid CO_2 acceptors at high temperatures and particularly Na_2ZrO_3 is a candidate to compete with current synthetic sorbents reported in literature such as Li_4SiO_4 and Li_2ZrO_3.[10,14] The use of sodium as a raw material for the preparation of synthetic CO_2 sorbents at high temperatures could result in more economic manufacture of these materials and related applications, since lithium oxides generally have higher costs than sodium-based oxides.

Experimental data showed that Na_2ZrO_3 can absorb almost 100% of the maximum theoretical CO_2 sorption compared to 70% and 80% of Li_2ZrO_3 and Li_4SiO_4, respectively. Also Na_2ZrO_3 experimental data presented the highest sorption rate compared to current related sorbents (Li_4SiO_4 and Li_2ZrO_3). However, regeneration performance was not as good as Li_4SiO_4 and

Li_2ZrO_3. In a two-cycle run Na_2ZrO_3 showed good sorption and regeneration performance. The lower regeneration rate observed with this sorbent, particularly towards the end of regeneration can be improved with the use of an eutectic mixture of Na/K carbonates as described by Ichi Ida and Lin,[14] which provide a liquid mixture inter-phase to promote CO_2 diffusion out of the particle during regeneration. Other options are to work with dopants such as Li and Y as discussed by J.-i. Ida et al.,[16] and provide a single liquid phase to promote the CO_2 diffusion in the particle. This phenomenon resulted in improved regeneration properties in the authors Li_2ZrO_3 sorbents. We are presently working in our laboratory to synthesize Na_2ZrO_3 through other methods such as coprecipitacion to reduce the particle size of the material and to modify it with the options pointed out above. Results will be reported in following publications.

Other applications for Na_2ZrO_3 may involve the use of this material for the development of inorganic membranes for CO_2 separation as described by Ichi Ida and Lin[14] and Yoshida.[4] Finally the mechanism or model of sorption and regeneration of Na_2ZrO_3 needs to be understood in order to formulate materials with better CO_2 sorption properties at high temperatures.

ACKNOWLEDGMENTS

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