

NOVEL CARBON DIOXIDE SOLID ACCEPTORS USING SODIUM CONTAINING OXIDES

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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 (CO₂) to the atmosphere creating environmental problems such as global climate warming. In the near future Industry, if mandated to remove CO₂, will certainly require improved and novel technologies for the efficient removal of CO₂. 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 CO₂ emissions to the atmosphere. Among such technologies is the use of the CO₂ sequestration concept that in many cases has proven to be an alternative (Draper and Becker, 2000). Examples of such processes are: the CO₂ capture during coal gasification (Hoffman and Pennline, 2000), the sorption enhanced reaction (SER) for the production of hydrogen (Lopez-Ortiz and Harrison, 2001) and the use of inorganic membranes for CO₂ separation in molten carbonate fuel cells (MCFC) (Yoshida, 1994).

The use of solid acceptors for CO₂ sequestration have been widely used in the past and started many years ago for the CO₂ separation in the coal gasification process (Curran et al, 1967). Several investigators examined the effects of temperature, pressure, and reactive gas composition of calcium oxide (CaO) based materials using thermo-gravimetric (TGA) reactor techniques (Silaban and Harrison, 1996, Han and Harrison, 1997). 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 (Silaban and Harrison, 1996). However, high regeneration temperatures were needed (950°C) using this acceptor of mineral nature. Also of mineral origin hidrotalcites (Mg₆Al₂(CO₃)(OH)₁₆·4H₂O) were used by Hufton et al (1999) and Ding and Alpay, (2001) at relatively high temperatures 400-550°C. However the sorption capacity of these hidrotalcites were low.

Recently, Ohashi et al (2001) developed a novel synthetic CO₂ separation technique by using lithium zirconate (Li₂ZrO₃) as a solid CO₂ 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 (LiFeO₂), lithium nickel (LiNiO₂), lithium titanate (Li₂TiO₃), lithium methasilicate (Li₂SiO₃) and lithium orthosilicate (Li₄SiO₄) used at various temperatures (Masahiro et al, 2002). Certainly, among all these Li₄SiO₄ was found to have the highest capacity and reactivity with CO₂ (Masahiro et al, 2001)

It was also reported that potassium carbonate dispersed on Li₂ZrO₃ added as a promoter increased the sorption rate compared to Li₂ZrO₃ alone (Nakagawa and Ohashi, 1998). Ichi Ida and Lin (2003) and Ohashi et al (1999) explained with the use of a reaction model TGA-DSC data how such carbonates formed an eutectic mixture of lithium carbonate and potassium carbonate (Li₂CO₃-K₂CO₃) that helped to improve Li₂ZrO₃ sorption kinetics.

Ohashi et al (2001) also used other alkali carbonates as promoters for Li₂ZrO₃ sorption kinetics. Examples of such promoters used by Ohashi et al were sodium carbonate (Na₂CO₃), potassium carbonate (K₂CO₃), magnesium carbonate (MgCO₃) and calcium carbonate (CaCO₃). However, sodium oxides by themselves have not been reported to have a significant high-temperature sorption performance (greater than 400°C). Sodium carbonates and oxides were only reported to show promoting effects on Li₂ZrO₃ and Li₄SiO₄ added in a maximum amount of 30% mol (Masahiro et al, 2002). This paper reports the use of novel CO₂ acceptors using sodium-containing oxides in the temperature range of 600-700°C. The oxides described here react reversibly with CO₂ through the following reaction:



where Na₂MeO₃ represents a sodium oxide such as sodium antimonite (Na₃SbO₄), sodium titanate (Na₂TiO₃) and sodium zirconate (Na₂ZrO₃). In this study we examine the CO₂ sorption and desorption characteristics of these oxides with the help of thermogravimetric analysis (TGA), X-ray diffraction (XRD), particle size and density.

EXPERIMENTAL SECTION

Synthesis and Characterization of Na-Oxides

Na₂ZrO₃, Na₂TiO₃ and Na₃SbO₄ were prepared by the solid-state method. Stoichiometric lithium zirconate (Li₂ZrO₃-F14) and lithium orthosilicate (Li₄SiO₄-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 performed as follows: 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 Na₂ZrO₃-F61 that used a 10% excess of sodium carbonate. The mixtures were calcined at temperatures reported in Table 1 for 4 hours

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 $10\ \mu\text{m}$. 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 $4.0\ \text{g/cm}^3$ with the exception of Li_4SiO_4 (F66), which had a lower density of $2.2\ \text{g/cm}^3$.

Table 1. Synthesized Sorbents Prepared by Solid State Method

Sample	Precursors	Molar Ratio	Calcination Temperature	Density g/cm^3	Average Particle Size μm
Na_2TiO_3 -F41	TiO_2 : Na_2CO_3	1:1	700°C	3.14	3.22
Na_3SbO_4 -F54	Sb_2O_3 : Na_2CO_3	1:1	950°C	4.15	4.23
Na_2ZrO_3 -F34A	Ac Ac Zr: Na_2CO_3	1:1	800°C	4.25	7.84
Na_2ZrO_3 -F61	Ac Ac Zr: Na_2CO_3	1:1.1	900°C	4.74	5.25
Li_2ZrO_3 -F14	Ac Ac Zr: Li_2CO_3	1:1	950°C	3.87	4.62
Li_4SiO_4 -F66	SiO_2 : LiOOCCH_3	1:1	950°C	2.22	8.36

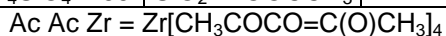


Figure 1 shows the XRD patterns of the synthesized acceptors: Na_2ZrO_3 -F34A, Na_2ZrO_3 -F61, Li_2ZrO_3 -F14 and Li_4SiO_4 -F66. Most of the XRD patterns in Figure 1 show pure phases after calcination. Na_2ZrO_3 -F34A pattern shows some unreacted ZrO_2 peaks still present in the sample. Preparing Na_2ZrO_3 -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_2ZrO_3 -F61 showed no impurities at all. Also some small peaks corresponding to ZrO_2 were found in sample Li_2ZrO_3 -F14. However, the presence of small quantities of ZrO_2 in Li_2ZrO_3 is believed to not influence the sorption performance of this sample (Ohashi et al, 2001).

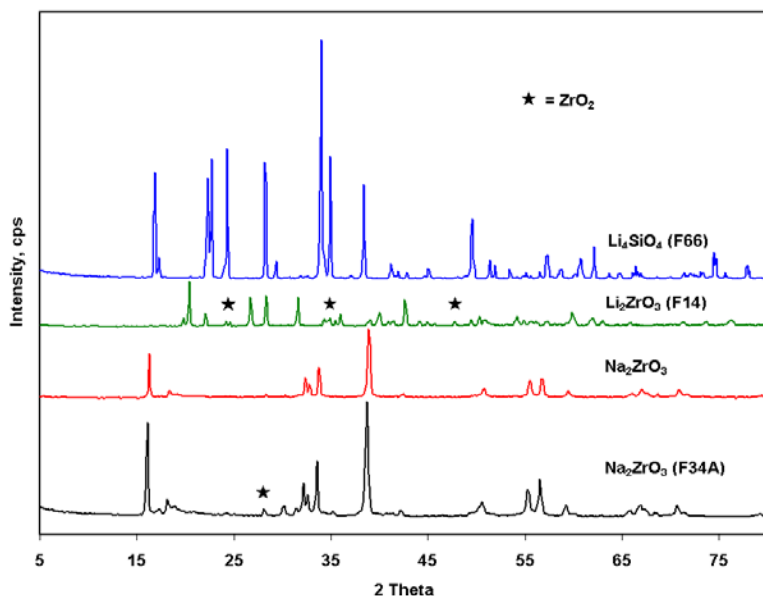


Figure 1. XRD Patterns of Synthesized Na-based Oxides

Figure 2 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

Figure 2 shows the XRD patterns of samples

unwanted crystal phases. However, poor-reactive high molecular weight titanates such as $\text{Na}_8\text{Ti}_5\text{O}_{14}$ were produced.

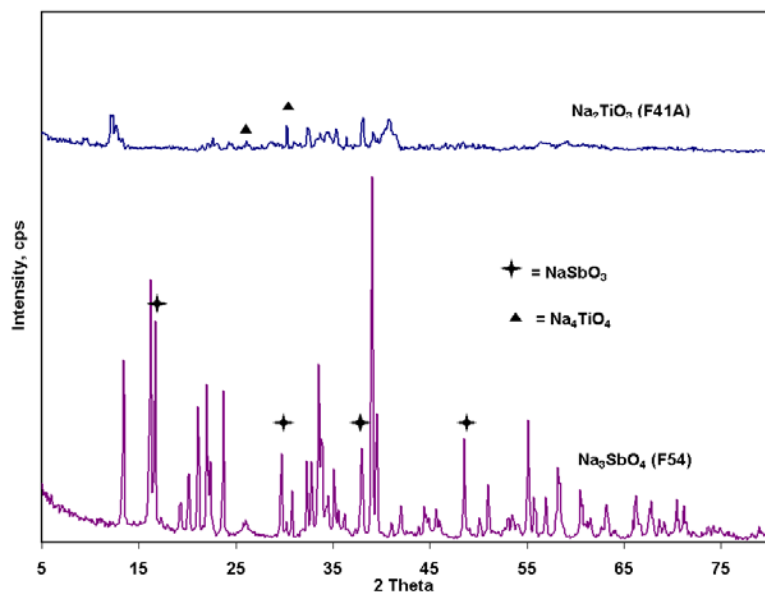


Figure 2. XRD Patterns of Samples F41A and F54

Results and Discussion

CO₂ 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 (Perking Elmer) to be tested for their CO₂ sorption-desorption performance. Passing UHP argon during heating up to the reaction temperature of 600°C for about 40 minutes dried the samples. Then, the CO₂ sorption reaction (1) started by

admitting a flow of 150 ml/min of 80% CO₂. After sorption was completed, the samples were heated to their corresponding regeneration temperature. During regeneration 850°C was used for Na₃SbO₄-F54, 780°C for Na₂ZrO₃-F34A and Na₂ZrO₃-F61 and 700°C for Na₂TiO₃-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.

Table 2. Sorption/Regeneration Performance of Synthesized CO₂ Acceptors

Sorbent	T Reg. °C	Sorption Rate %W/min	Regeneration Rate %W/min	CO ₂ Absorbed %	CO ₂ Released %	Max. Theoretical Sorption %
Li ₂ ZrO ₃ -F14	780	0.03	5.55	13.07	11.67	28.70
Na ₂ TiO ₃ -F41	700	0.11	0.04	8.00	10.00	26.00
Li ₄ SiO ₄ -F66	800	0.92	7.52	13.34	11.78	36.70
Na ₃ SbO ₄ -F54	850	2.47	2.01	14.50	14.50	20.40
Na ₂ ZrO ₃ -F34A	780	7.27	1.90	19.95	16.92	23.70
Na ₂ ZrO ₃ -F61	780	10.33	1.00	25.77	22.00	23.70

Figure 3 shows the CO₂ sorption TGA response of the Na-based sorbents. Sample Na₂TiO₃-F41 presented the lowest sorption with only 8% weight 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 CO₂ such as the one observed in the XDR pattern of Figure 2.

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

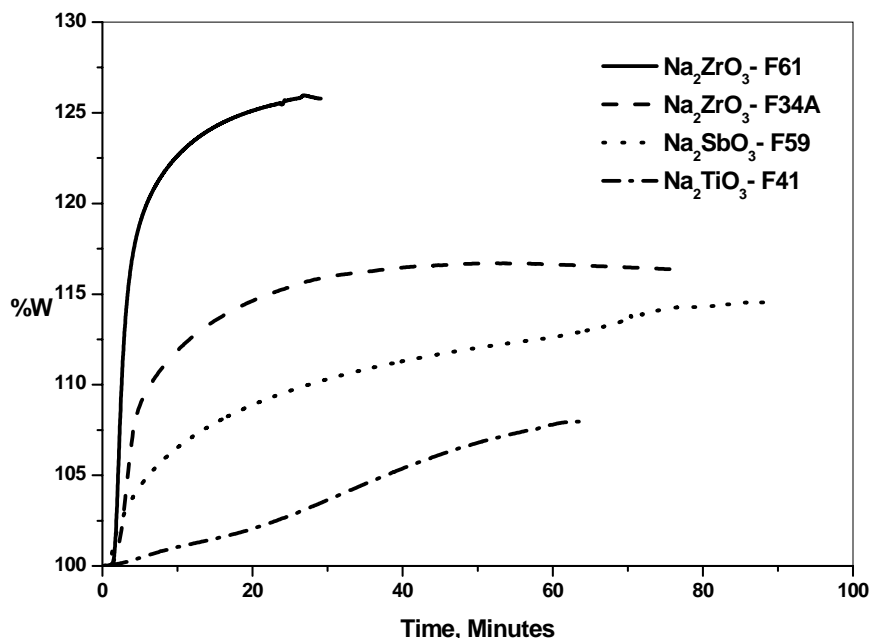


Figure 3. TGA Response of Synthesized Na-based Acceptors

Figure 3 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 7.27 %W/min and showed a CO_2 sorption of 19.95% which is about 84% 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 Figure 3. Sorbent Na_2ZrO_3 -F61 not only showed an improved sorption rate value of 10.33 %W/min (about 1.5 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 (2002) 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 minutes 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 minutes. 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 minutes (not shown in Figure 4) with a sorption rate also in

between the two previously reported sorbents. It is important to mention that our sorbent $\text{Na}_2\text{ZrO}_3\text{-F61}$ was not modified with the addition of a promoter for this test.

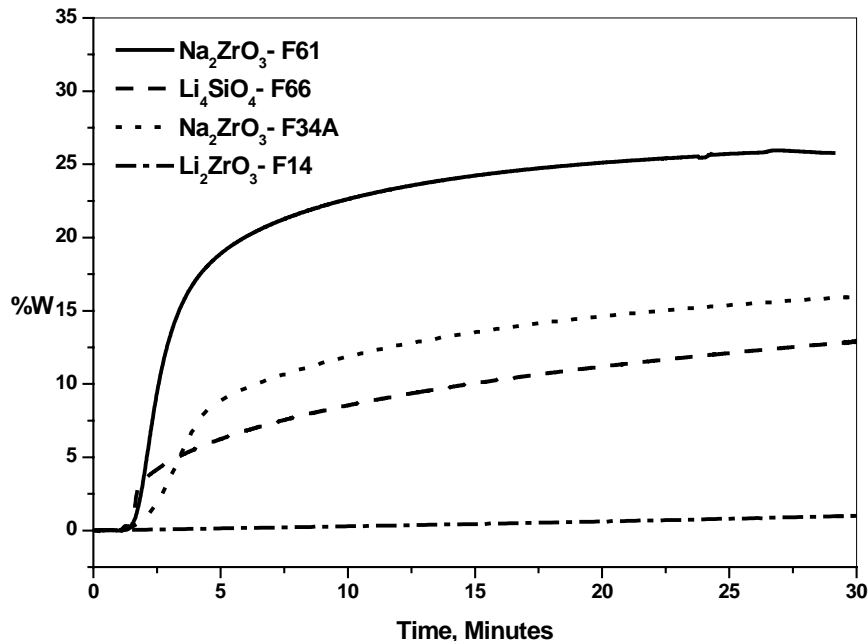


Figure 4. TGA Response for Sorbent Comparison at 600°C

tests are presented in Figure 4. From Figure 4 it can be seen that the highest sorption was achieved by $\text{Na}_2\text{ZrO}_3\text{-F61}$ with about 26%W, followed by $\text{Na}_2\text{ZrO}_3\text{-F34A}$ with 20%W and $\text{Li}_4\text{SiO}_4\text{-F66}$ with 13%W. Finally, $\text{Li}_2\text{ZrO}_3\text{-F14}$ only achieved with only 1%W. However, the slow sorption rate of this sample ended up with a %W of 13, only after 325 minutes (not shown in Figure 4).

Table 2 shows the sorption rate as observed in these tests. From these values and Figure 4 it is evident that the order from higher to lower sorption rate is as follows: $\text{Na}_2\text{ZrO}_3\text{-F61} > \text{Na}_2\text{ZrO}_3\text{-F34A} > \text{Li}_4\text{SiO}_4\text{-F66} > \text{Li}_2\text{ZrO}_3\text{-F14}$. Therefore, the highest sorption rate was achieved by $\text{Na}_2\text{ZrO}_3\text{-F61}$, which was about 1.5 times faster than $\text{Na}_2\text{ZrO}_3\text{-F34A}$ and almost eleven times faster than $\text{Li}_4\text{SiO}_4\text{-F66}$. Also it is evident the low performance of $\text{Li}_2\text{ZrO}_3\text{-F14}$ at these conditions. The previous results agreed with data reported by Masahiro et al (2001) 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 possesses significantly better rate sorption performance than Li_4SiO_4 .

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: $\text{Li}_4\text{SiO}_4\text{-F66} > \text{Li}_2\text{ZrO}_3\text{-F14} > \text{Na}_3\text{SbO}_4\text{-F54} > \text{Na}_2\text{ZrO}_3\text{-F34A} > \text{Na}_2\text{ZrO}_3\text{-F61} > \text{Na}_2\text{TiO}_3\text{-F41}$.

In order to better compare these sorbents $\text{Li}_4\text{SiO}_4\text{-F66}$ and $\text{Li}_2\text{ZrO}_3\text{-F14}$ (without promoter) were prepared at our 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 $\text{Na}_2\text{ZrO}_3\text{-F61}$. TGA tests were performed at 600°C and 100% CO_2 (as described previously) and comparison of these

Li₄SiO₄-F66 presented the highest regeneration rate with 7.5%W/min at 800°C. Li₄SiO₄ was also regenerated with only 1.5%W less than the amount absorbed. The next better regeneration rate was observed for Li₂ZrO₃-F14 with only 1.4%W less than the amount absorbed. This was followed by Na₃SbO₄-F54, which released the same amount of CO₂ absorbed. Na₂ZrO₃ sorbents showed a slower regeneration rate compared to the sorbents described above. Also the amount of CO₂ released was lower than the absorbed by these two samples. It is to note here that the excess in Na present in the sample Na₂ZrO₃-F61 was not fully regenerated. This may explain why the amount of CO₂ released (22%W) was much lower than the absorbed (25%W). This behavior is the most troubling for the Na₂ZrO₃ acceptor and it is yet to be studied in further experimental work, which may involve the addition of a promoter of the reaction/regeneration rate (Ohashi and Nakagawa, 1999). Finally Na₂TiO₃-F41 showed the lowest regeneration rate. The fact that the amount of CO₂ 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 feasible it is needed for the sorbent to be subjected through sorption and regeneration cycles. Figure 5 shows two sorption/regeneration cycles of Na₂ZrO₃-F61. During the first cycle F61 absorbs 25.6%W at a temperature of 600°C. After the first sorption was completed temperature

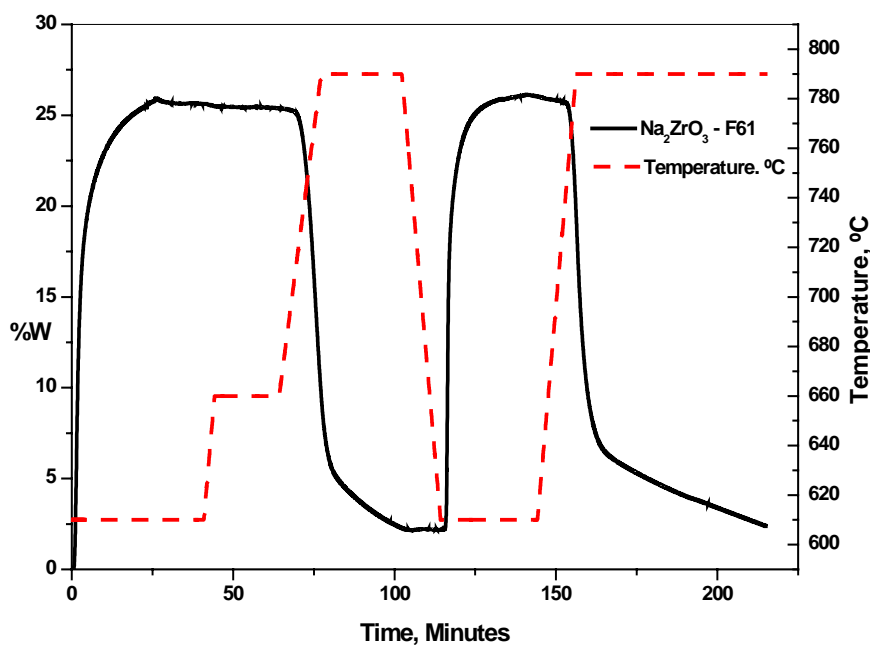


Figure 5. Two-Cycle Response of Sample Na₂ZrO₃-F61

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 pure Na₂ZrO₃, 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

(Na₂CO₃) and without free ZrO₂, regeneration of this excess carbonate would not be possible, since regeneration of pure Na₂CO₃ 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 Na₂ZrO₃-F61 is the slow final rate observed during regeneration that is particularly slower in the case of the second cycle. This behavior was observed before during regeneration of sorbents F34A and F61. It is possible that diffusion of CO₂ through Na₂CO₃ 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 CO₂ sorption at high temperatures ($T > 400^{\circ}\text{C}$) have been reported in literature only as promoters of Li₂ZrO₃ and Li₄SiO₄, but never as CO₂ sorbents as themselves (Ohashi et al, 2001). The novelty of this research is based in the fact that Na-oxides are able to capture CO₂ at high temperatures (600°C), which make these kind of oxides particularly attractive for applications such as inorganic membranes for CO₂ separation in molten carbonate fuel cells (MCFC) (Yoshida, 1994).

As Na-based sorbents, the highest activity towards CO₂ sorption was presented by Na₂ZrO₃, followed by Na₃SbO₄ and finally by Na₂TiO₃.

The use of a 10% excess of sodium in Na₂ZrO₃ was responsible for the increase in purity, reactivity and sorption capacity compared to stoichiometric Na₂ZrO₃.

Na-based sorbents can be used as an alternative for solid CO₂ acceptors at high temperatures and particularly Na₂ZrO₃ is a candidate to compete with current synthetic sorbents reported in literature such as Li₄SiO₄ and Li₂ZrO₃ (Ohashi, 2001, Ichi Ida and Lin, 2003). The use of sodium as a raw material for the preparation of synthetic CO₂ sorbents at high temperatures could result in more economic manufacture of these materials in related applications, since lithium oxides generally have higher costs than sodium-based oxides.

Experimental data showed that Na₂ZrO₃ can absorb almost 100% of the maximum theoretical CO₂ sorption compared to about 40% for both Li₂ZrO₃ and Li₄SiO₄. Also Na₂ZrO₃ experimental data presented the highest sorption rate compared to current related sorbents (Li₄SiO₄ and Li₂ZrO₃). However, regeneration performance was not as good as Li₄SiO₄ and Li₂ZrO₃. In a two-cycle run Na₂ZrO₃ 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 a promoter as described by Ichi Ida and Lin (2003), which may provide a liquid mixture inter-phase to promote CO₂ diffusion out of the particle during regeneration. Other options are to work with dopants such as Y as discussed by J.-i. Ida et al (2004), and provide a single liquid phase to promote the CO₂ diffusion in the particle. This phenomenon resulted in improved regeneration properties in the authors Li₂ZrO₃ sorbents. We are presently working in our laboratory to synthesize Na₂ZrO₃ through other methods such as coprecipitation 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.

Applications for Na₂ZrO₃ may involve the use of this material for the development of inorganic membranes for CO₂ separation as described by Ichi Ida and Lin (2003) and Yoshida (1994). Finally the mechanism or model of sorption and regeneration of Na₂ZrO₃ needs to be understood in order to formulate materials with better CO₂ sorption properties at high temperatures.

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