Novel High Temperature CO_2 Acceptor Using Zirconium-Based Alkali Mixed Oxides

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Introduction

World economy at present relies on burning fossil fuels to produce affordable energy. A consequence of the use of these fuels is the emission of large amounts of carbon dioxide (CO_2) to the atmosphere creating environmental problems such as global climate warming. In the near future, if CO_2 emission regulations are enforced, industry will require improved technologies for the efficient capture of CO_2. Examples of such processes are high temperature 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 molten carbonate fuel cells (MCFC) [4].

Solid acceptors for CO_2 capture have been widely used in the past for CO_2 separation in the coal gasification process [5]. Several investigators examined the effects of temperature, pressure, and reactive gas composition on calcium oxide (CaO) based materials using thermo-gravimetric (TGA) reactor techniques [6,7]. However, degradation (sintering) of these materials was observed during multicycle tests. Calcined dolomite ($MgCO_3*CaCO_3$) proved to be superior in multicycle performance to previous CaO based past materials [6]. However, high regeneration temperatures were needed (950°C) for this acceptor. Bandi [8] reported improved multicycle performance using the mineral Huntite ($Mg_3Ca(CO3)_4$). However, high regeneration temperatures again were the drawback. Hydrotalcites ($Mg_6Al_2(CO_3)(OH)_{16} \cdot 4H_2O$) were used by Hufton et al [9] and Ding and Alpay [10] at relatively high temperatures 400-550°C. However the sorption capacity of these hydrotalcites was low.

Within the past four years a new generation of synthetic acceptors evolved from the work from Ohashi et al [11], who developed a novel CO_2 separation technique by using regenerable lithium zirconate (Li_2ZrO_3) as a solid CO_2 acceptor in the temperature range of 450-700°C. The main advantages of this material were: lower regeneration temperature (810°C) compared to calcium-based acceptors. The improved thermal stability allowed an increased number of sorption/regeneration cycles without loosing its capture capacity. However, the sorption rate of Li_2ZrO_3 was very slow. Kato et al [12] proposed other acceptors based on lithium such as: lithium ferrite ($LiFeO_2$), lithium nickelite ($LiNiO_2$), lithium titanate (Li_2TiO_3), lithium methasilicate (Li_2SiO_3) and lithium

orthosilicate (Li_4SiO_4). Among these Li_4SiO_4 was found to posses the highest capacity (28% higher than Li_2ZrO_3) and sorption rate with CO_2. Kato et al. [12] exposed Li_4SiO_4 to 50 sorption-regeneration cycles without loosing its sorption capacity. However the weight increase during carbonation was only about 82% of its theoretical maximum capacity.

This new generation of synthetic high temperature CO_2 acceptors, which posses good acceptor regeneration and exceptional stability features is based on mixtures of oxides with Li as their main component. In previous studies, in our laboratory, we synthesized CO_2 acceptor mixtures based on Na oxides [13] and we observed that sodium zirconate (Na_2ZrO_3) produced similar or even superior CO_2 sorption performance properties compared to Li based oxides [2,4]. The sorption mechanism was based upon the following reaction (1):

$$Na_2ZrO_3 + CO_2 \Leftrightarrow Na_2CO_3 + ZrO_2 \qquad (1)$$
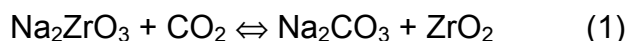
In that study it was found that Na_2ZrO_3 showed superior sorption kinetics compared to lithium based acceptors Li_2ZrO_3 and Li_4SiO_4 [14]. However, the success of any CO_2 acceptor depends on its multicycle durability, which the material under consideration, Na_2ZrO_3, is lacking. Na_2ZrO_3 regeneration problems were encountered towards the final portion of the regeneration step, which was associated with a diffusion resistance within the particle not allowing CO_2 to be easily removed during regeneration. This regeneration problem was even more accentuated as the number of cycles increased.

In a recent work, aiming to solve this regeneration problem, mixtures of Li_2ZrO_3 and Na_2ZrO_3 were prepared and characterized by Pfeiffer et al. [15]. They propose that the ability of Li_2ZrO_3 and Na_2ZrO_3 to capture CO_2 at high temperatures resides in the mobility of lithium or sodium in their crystal structures constituted by ZrO_3^{-2}. They established that diffusion of sodium or lithium is determined by the structure and morphology of the compounds in those mixtures. They suggested that these mixtures could present fast sorption/regeneration kinetics. However, they did not report any CO_2 capture evaluation of those mixtures.

The objective of the present work is to study the CO_2 capture of mixtures of Na_2ZrO_3/Li_2ZrO_3 acceptors at high temperatures and to determine the optimal Na_2ZrO_3/Li_2ZrO_3 molar ratio to insure fast enough sorption/regeneration kinetics with the use of thermogravimetric (TGA), and X-ray diffraction (XRD) analysis.

Experimental
In this research mixtures of Na_2ZrO_3/Li_2ZrO_3 acceptors were synthesized through the impregnated suspension method (SI) [16], which consists in suspending one of the solid precursors in a liquid medium, such as distilled water, and simultaneously incorporate an aqueous solution of a dissolved salt of the other precursor, while heating and maintaining constant stirring of the system until complete evaporation. Finally, the dried mixture is calcined to a previously determined synthesis temperature.

The mixtures were synthesized starting from an aqueous solution of $LiNO_3$ and $NaNO_3$ which was previously prepared by reacting stoichiometric amounts of reagent grade

Li_2CO_3/Na_2CO_3 (Sigma Aldrich) with 65.5% HNO_3 (J.T. Baker), and an aqueous solid suspension of ZrO_2 (Spectrum Chemical Mfg. Corp.). The Li/Na molar ratios used in the mixtures were: 9:1, 1.5:1, 1:1, 1:1.5 and 1:9 and named LiNa-9, LiNa-3/2, LiNa-1, LiNa-2/3 and LiNa-1/9, respectively. These samples were dried and later calcined at 900° in an air heated Thermolyne F-6000 oven for 4 hours.

Characterization

Characterization of the samples consisted in X-ray diffraction (XRD). Diffraction patterns were obtained on a Phillips XPERTMPD with CuKα. The CO_2 sorbent activity performance was evaluated through thermogravimetric analysis (TGA), System-Pyris-1 Perkin-Elmer. TGA test conditions for the experimental evaluation were: 600°C, 80 mol% CO_2/Ar and 150 sccm, while regeneration used 850°C in air at 100 sccm.

Results and Discussion

XRD results for all Na_2ZrO_3/Li_2ZrO_3 acceptors are shown in Figure 1. Na_2ZrO_3 and Li_2ZrO_3 diffraction patterns were included for comparison purposes.

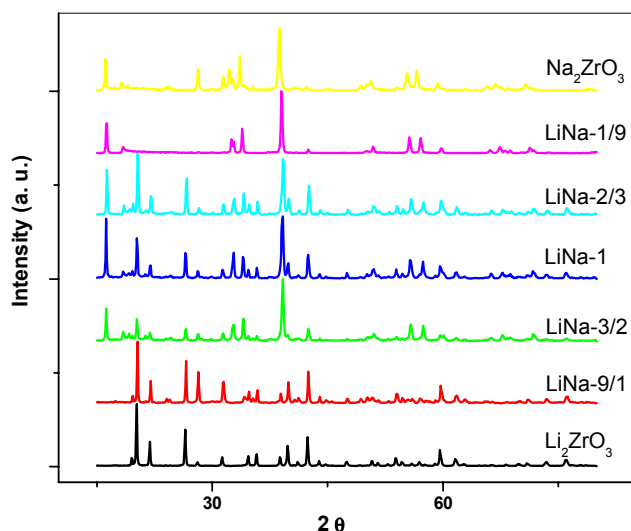Figure 1. XRD results of synthesized Na_2ZrO_3/Li_2ZrO_3 acceptors

Sample LiNa-1/9 presents a slight shift in the entire diffraction pattern towards greater 2-theta values with respect to Na_2ZrO_3 characteristic peaks (presumably, $NaLiZrO_3$), while, sample LiNa-9/1 also shows a smaller difference shift of the characteristic Li_2ZrO_3 diffraction pattern (presumably, $LiNaZrO_3$). This shifting behavior can be attributed to a decrease in the inter-planar distance of the crystalline structure either of Na_2ZrO_3 or Li_2ZrO_3, resulting from a substitution of some of the Na by Li atoms in sample LiNa-1/9 and Li by Na atoms in sample LiNa-9/1, respectively [17]. Finally, samples LiNa-2/3, LiNa-1 and LiNa-3/2 show both Na_2ZrO_3 and Li_2ZrO_3 crystal structures. The diffraction patterns of these samples show the same pattern displacement as the ones exhibited by samples LiNa-1/9 and LiNa-9/1, respectively. These XRD results agree with findings of Pfeiffer et al. [15].

Figure 2 presents TGA CO_2 sorption results of all the synthesized samples in the present study.
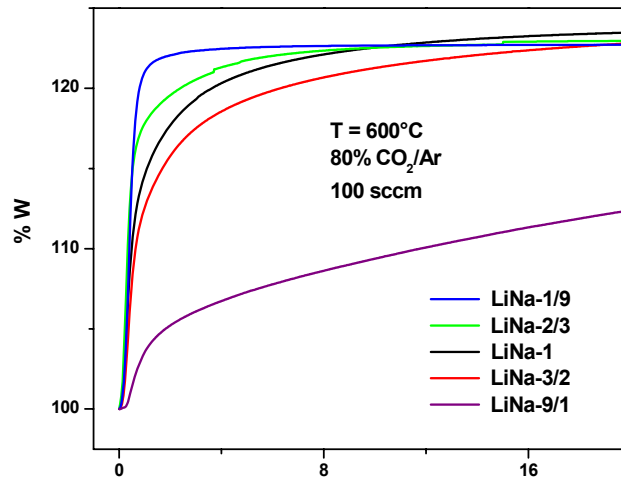
Figure 2. TGA CO_2 sorption results of synthesized Na_2ZrO_3/Li_2ZrO_3 acceptors

In this plot it is evident that the order from fast to slow sorption kinetics is as follows: LiNa-1/9 > LiNa-2/3 > LiNa-1 > LiNa-3/2 > LiNa-9/1. This behavior indicates that as sodium is present in greater amounts in the mixtures the sorption kinetics gradually increases. This is consistent with results obtained by Lopez et al. and Bok Yi and Eriksen [13, 18]. They found that Na_2ZrO_3 presented the fastest CO_2 sorption kinetics compared to Li_2ZrO_3. Another interpretation of results in Figure 2 is that Li_2ZrO_3 generates slow sorption kinetics and these are even more reduced as the Li content in the mixture is increased. Therefore, we can conclude that fast and slow sorption kinetics are associated with the Na and Li content in the mixture, respectively. While, intermediate Li and Na contents fall in between these kinetics.

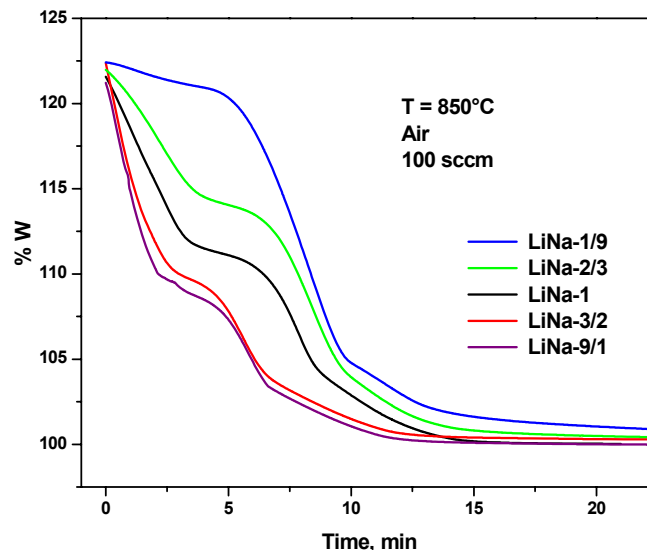Figure 3 presents TGA CO_2 regeneration results of all the synthesized samples in the present study.

Figure 3. TGA regeneration results of synthesized Na_2ZrO_3/Li_2ZrO_3 acceptors

From this Figure the order in which regeneration take place from fast to slow kinetics is the following: LiNa-9/1 > LiNa-3/2 > LiNa-1 > LiNa-2/3 > LiNa-1/9. This result is exactly the opposite order to the sorption kinetics and provides in principle, that the greater the

Li content in the mixture, the faster the regeneration kinetics. However, there is a strange slow transitional behavior that all the mixtures exhibit either in the beginning, the middle or towards the end of the regeneration process. This slow transition generates a delay in the regeneration kinetics and is though to be associated with the change in sorption regions governed by either Na_2ZrO_3 or Li_2ZrO_3 and their substituted $LiNaZrO_3$ (Na into Li_2ZrO_3 structure) and $NaLiZrO_3$ (Li into Na_2ZrO_3 structure) mixtures.

Pfeiffer et al. [15] have proposed that the formation of these substituted mixtures are due to the solubility limit of sodium into Li_2ZrO_3, which is of Li/Na = 9 (LiNa-9/1) and by the solubility limit of Li into Na_2ZrO_3 that is Li/Na = 7/3. However, XRD results reveal that even though for ratios of Li/Na $\leq$ 2/3 (LiNa-2/3) both crystal structures of $LiNaZrO_3$ and $NaLiZrO_3$ are present in the diffraction pattern. Therefore, this implies that even though the solubility limit of Li into Na in Na_2ZrO_3 is not reached, both structures may be present at all times. This is not true for the case of the substitution of Na into Li in Li_2ZrO_3, since for values of Li/Na $\geq$ 9 (LiNa-9/1) since the only crystal structure present in the diffraction pattern is Li_2ZrO_3. However, small quantities of Na_2ZrO_3 can be present in those mixtures that presumably are not able to be detected by XRD analysis.

It is possible that these kinetic transition delays could be attributed to difusional limitations in the regions where structures of $LiNaZrO_3$ or $NaLiZrO_3$ are present. These limitations can be associated to the packing of the crystal structures caused by the atom substitutions that may consequently hinder the CO_2 evolution process during regeneration of the mixture [15].

Another important issue that needs to be addressed is the fact that the period in time of the above mentioned transition delay in regeneration kinetics (as observed in Figure 3) is increased as the amount of Na is also increased in these mixtures. Since pure Na_2ZrO_3 has been reported to present slower regeneration kinetics than Li_2ZrO_3 [13, 18] it is expected that a greater amount Na content may be traduced in slower regeneration kinetics in a mixture acceptor.

Considering both sorption and regeneration processes it can be concluded that sample LiNa-1 (Li/Na = 1) is the one that presents a reasonable balance between sorption and regeneration kinetics. Finally, more conclusive experimental tests are needed to elucidate which substituted $LiNaZrO_3$ or $NaLiZrO_3$ structure is responsible for the transition delay during regeneration of the acceptors. These tests may include molecular simulations and XRD-Rietveld analysis to determine the exact crystal structure of these mixtures as Na and Li content is varied and those related to the CO_2 sorption/regeneration performance.

Conclusions

According to XRD results, The studied mixtures of Na_2ZrO_3 and Li_2ZrO_3 resulted in substitution of some Na into Li_2ZrO_3 ($LiNaZrO_3$) and Li into Na_2ZrO_3 ($NaLiZrO_3$) crystal structures. The degree of those substitutions was found to be determined by the solubility limits of Li and Na in those structures.

According to TGA CO_2 sorption experiments of the mixture acceptors, the order from fast to slow sorption kinetics was as follows: LiNa-1/9 > LiNa-2/3 > LiNa-1 > LiNa-3/2 > LiNa-9/1 while, regeneration kinetics resulted in the opposite behavior.

During regeneration of the mixtures a strange slow transitional behavior was found to generate a delay in the regeneration kinetics and this was associated with their substituted $LiNaZrO_3$ (Na into Li_2ZrO_3 structure) and $NaLiZrO_3$ (Li into Na_2ZrO_3 structure) structures. The period in time of the transition delay in regeneration kinetics was increased as the amount of Na was also increased in the mixtures.

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More conclusive experimental tests are needed to elucidate which substituted structure is responsible for the transition delay during regeneration of the acceptors.

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