Novel High Temperature CO₂ 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 (CO₂) to the atmosphere creating environmental problems such as global climate warming. In the near future, if CO₂ emission regulations are enforced, industry will require improved technologies for the efficient capture of CO₂. Examples of such processes are high temperature CO₂ capture during coal gasification [2], the sorption enhanced reaction (SER) for the production of hydrogen [3] and the use of inorganic membranes for CO₂ separation in molten carbonate fuel cells (MCFC) [4].

Solid acceptors for CO₂ capture have been widely used in the past for CO₂ 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 (MgCO₃*CaCO₃) 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 Hunteite (Mg₃Ca(CO₃)₄). However, high regeneration temperatures again were the drawback. Hydrotalcites (Mg₆Al₂(CO₃)(OH)₁₆·₄H₂O) 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 CO₂ separation technique by using regenerable lithium zirconate (Li₂ZrO₃) as a solid CO₂ 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 Li₂ZrO₃ was very slow. Kato et al [12] proposed other acceptors based on lithium such as: lithium ferrite (LiFeO₂), lithium nickelite (LiNiO₂), lithium titanate (Li₂TiO₃), lithium methasilicate (Li₂SiO₃) and lithium
orthosilicate (Li$_4$SiO$_4$). Among these Li$_4$SiO$_4$ was found to possess the highest capacity (28% higher than Li$_2$ZrO$_3$) and sorption rate with CO$_2$. Kato et al. [12] exposed Li$_4$SiO$_4$ to 50 sorption-regeneration cycles without losing 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 possess 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$_2$ZrO$_3$) 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):

$$\text{Na}_2\text{ZrO}_3 + \text{CO}_2 \leftrightarrow \text{Na}_2\text{CO}_3 + \text{ZrO}_2 \quad (1)$$

In that study it was found that Na$_2$ZrO$_3$ showed superior sorption kinetics compared to lithium based acceptors Li$_2$ZrO$_3$ and Li$_4$SiO$_4$ [14]. However, the success of any CO$_2$ acceptor depends on its multicycle durability, which the material under consideration, Na$_2$ZrO$_3$, is lacking. Na$_2$ZrO$_3$ 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$_2$ZrO$_3$ and Na$_2$ZrO$_3$ were prepared and characterized by Pfeiffer et al. [15]. They propose that the ability of Li$_2$ZrO$_3$ and Na$_2$ZrO$_3$ 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$_2$ZrO$_3$/Li$_2$ZrO$_3$ acceptors at high temperatures and to determine the optimal Na$_2$ZrO$_3$/Li$_2$ZrO$_3$ 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$_2$ZrO$_3$/Li$_2$ZrO$_3$ 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
Li₂CO₃/Na₂CO₃ (Sigma Aldrich) with 65.5% HNO₃ (J.T. Baker), and an aqueous solid suspension of ZrO₂ (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 CO₂ 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% CO₂/Ar and 150 sccm, while regeneration used 850°C in air at 100 sccm.

Results and Discussion
XRD results for all Na₂ZrO₃/Li₂ZrO₃ acceptors are shown in Figure 1. Na₂ZrO₃ and Li₂ZrO₃ diffraction patterns were included for comparison purposes.

[Figure 1: XRD results of synthesized Na₂ZrO₃/Li₂ZrO₃ acceptors]

Sample LiNa-1/9 presents a slight shift in the entire diffraction pattern towards greater 2-theta values with respect to Na₂ZrO₃ characteristic peaks (presumably, NaLiZrO₃), while, sample LiNa-9/1 also shows a smaller difference shift of the characteristic Li₂ZrO₃ diffraction pattern (presumably, LiNaZrO₃). This shifting behavior can be attributed to a decrease in the inter-planar distance of the crystalline structure either of Na₂ZrO₃ or Li₂ZrO₃, 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 Na₂ZrO₃ and Li₂ZrO₃ 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 CO₂ sorption results of all the synthesized samples in the present study.
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 Na₂ZrO₃ presented the fastest CO₂ sorption kinetics compared to Li₂ZrO₃. Another interpretation of results in Figure 2 is that Li₂ZrO₃ 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 CO₂ regeneration results of all the synthesized samples in the present study.

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$_2$ZrO$_3$ or Li$_2$ZrO$_3$ and their substituted LiNaZrO$_3$ (Na into Li$_2$ZrO$_3$ structure) and NaLiZrO$_3$ (Li into Na$_2$ZrO$_3$ 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$_2$ZrO$_3$, which is of Li/Na = 9 (LiNa-9/1) and by the solubility limit of Li into Na$_2$ZrO$_3$ 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$_2$ZrO$_3$ 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$_2$ZrO$_3$, since for values of Li/Na \(\geq 9\) (LiNa-9/1) since the only crystal structure present in the diffraction pattern is Li$_2$ZrO$_3$. However, small quantities of Na$_2$ZrO$_3$ 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$_2$ZrO$_3$ has been reported to present slower regeneration kinetics than Li$_2$ZrO$_3$ [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$_2$ZrO$_3$ and Li$_2$ZrO$_3$ resulted in substitution of some Na into Li$_2$ZrO$_3$ (LiNaZrO$_3$) and Li into Na$_2$ZrO$_3$ (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 CO₂ 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 LiNaZrO₃ (Na into Li₂ZrO₃ structure) and NaLiZrO₃ (Li into Na₂ZrO₃ 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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