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Research Article

Carbon Dioxide Adsorption by Calcium Zirconate at Higher Temperature

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Abstract

The CO_2 adsorption by calcium zirconate was explored at pre- and post- combustion temperature condition. The several samples of the calcium zirconate were prepared by different methods such as sol-gel, solid-solid fusion, template and micro-emulsion. The samples of the calcium zirconate were characterized by measurement of surface area, alkalinity/acidity, and recording the XRD patterns and SEM images. The CO_2 adsorptions by samples of the calcium zirconate were studied in the temperature range 100 to 850 ^{o}C and the CO_2 adsorptions were observed in the ranges of 6.88 to 40.6 wt % at 600 ^{0}C and 8 to 16.82 wt% at in between the temperatures 200 to 300 ^{o}C. The effect of Ca/Zr mol ratio in the samples of the calcium zirconate on the CO_2 adsorption and alkalinity were discussed. The adsorbed moisture by the samples of the calcium zirconate was found to be useful for the CO_2 adsorption. The promoted the samples of the calcium zirconate by K^+, Na^+, Rb^+, Cs^+, Ag^+ and La^{3+} showed the increased CO_2 adsorption. The exposure time of CO_2 on the samples of the calcium zirconate showed the increased CO_2 adsorption. The samples of the calcium zirconate were found to be regenerable and reusable several times for the adsorption of CO_2 for at the post- and pre-combustion temperature conditions.

Keywords: Calcium zirconate; CO_2 adsorption; effect of mol ratio; post- and pre-combustion temperature; sol-gel method

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1. Introduction

The carbon in the form of carbonate, hydrocarbons, and carbon dioxide, etc is found in the earth crust and atmosphere. However, carbonates and hydrocarbons are natural resources useful for the construction, chemical industry, fuel, etc. Trees are using large amount of CO_2 from the atmosphere for their growth. However, the emitted CO_2 from the outward sources such as vehicles, air craft's, thermal power station, animals, factories etc are the causes of surplus CO_2 in the atmosphere. The surplus CO_2 in the atmosphere causes the damage of biosphere by natural imbalance, global warming and air pollution. Therefore, there is a need to reduce the emission of CO_2 in the atmosphere or to develop the technology to store the CO_2 at the point of emission sources and then utilize it for development of value added products. The mixed metal oxides are emerged as the regenerable adsorbents for CO_2 at higher temperature.

The emission of CO_2 from the thermal power

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stations, vehicles, air craft's and industries are observed in the temperature ranges 100 to 450⁰C (post combustion conditions) and 450 to 850⁰C (pre-combustion conditions). The mixed metal oxides are suitable, stable and regenerable adsorbents for CO_2 at conditions of post- and pre- combustion temperatures. Among the adsorbents, zeolite, amines and carbon are used for CO_2 at low temperatures. However, these adsorbents lose their capacity for CO_2 with increasing in temperature [1-2]. MgO and CaO are CO_2 adsorbents at post- and pre- combustion temperatures; however, for achieving optimum CO_2 adsorption capacity is required high energy consumption by increasing temperature to 1000 °C [3-8]. Recently, lithium zirconate, silicate, aluminate [9-12], magnesium silicate, zirconate and aluminate [13-16], calcium silicate and aluminate [17-20] and calcium zirconate [21-26] were emerged as the regenerable adsorbents for CO_2 adsorption at low temperature. Mixed metal oxide catalysts are more favorable towards the hydrogenation of CO_2 than adsorption. However, alkali and alkaline earth metal oxide containing mixed metal oxide are more favorable towards the CO_2 adsorption. However, systematic investigations on CO_2 adsorption by calcium zirconate are lacking. Therefore, in this paper, we report the preparation of several samples of the calcium zirconate by different methods such as sol-gel, solid-solid fusion, template and micro-emulsion; characterization of the samples of the calcium zirconate and screening of samples of the calcium zirconate for CO_2 adsorption.

2. Materials and Methods

2.1. Chemical and apparatus

The chemicals calcium nitrate tetra hydrates, (S.D. Fine Chem. Pvt. Ltd), calcium carbonate, citric acid (Loba Cheme) were used to prepare calcium zirconate. All chemicals of analytical grade were used without any further purification. Carbon dioxide and helium of high purity were used (Deluxe India Ltd). A furnance (Thermax Co. Ltd) was used to calcine the calcium zirconate. A split furnace (Carbolite USA) was used to vary the temperature of the bed of the sample of the calcium zirconate adsorbent in the quartz reactor. The samples of the carbon dioxide were analyzed on line by using GC (Nucon India Ltd) with thermal conductivity detector.

2.2. The samples of the calcium zirconate preparation

The several samples of the calcium zirconate with variable Ca/Zr mol ratios from 0.5 to 6 were prepared by different methods such as sol-gel, solid-solid fusion, template and micro emulsion, etc. The details of the preparation of samples of the calcium zirconate by different methods are given in the following sections.

2.3. Preparation of samples of the calcium zirconate by sol-gel method

The several samples of the calcium zirconate with different mol ratios of Ca/Zr = 0.5, 1, 2, 3, 4 and 6 were prepared by sol gel method. Initially, for the preparation of samples of the calcium zirconate with Ca/Zr = 1 mol ratio, 0.0164, 0.0029 and 0.025 moles of citric acid, $Ca(NO_3)_2.4H_2O$ and urea, respectively, were dissolved in 2.56 mol of deionized water in a glass reactor. Then, 0.00145 mol of zirconly nitrate was added in the above solution with constant stirring. The solution was kept under constant heating at 70 ⁰C for 6 h. After that, the reaction mixture was digested on water bath at 80 ⁰C until the sol formation was completed. Then, the sol solution was thermally treated in a vaccum oven at 150 ⁰C in order to remove the excess water and to obtain the solid mass. Further, the solid mass was calcined in the furnace in air at 900 ⁰C for 3 h in order to obtain calcium zirconate crystalline phases. The particles of -22 to -30 mesh sizes were prepared from the calcined solid mass of the samples of the calcium zirconate.

2.4. Preparation of samples of the calcium zirconate by solid-solid fusion method

The samples of the calcium zirconate with different mol ratios of Ca/Zr = 0.5, 1, 2, 3, 4 and 6 were prepared by solid-solid fusion method. The samples of the calcium zirconate with Ca/Zr = 1 mol ratio were prepared by using 0.0058 and 0.023 moles of $CaCO_3$ and $ZrO(NO_3)_2$, respectively. The solid masses of $CaCO_3$ and $ZrO(NO_3)_2$ were thoroughly mixed together and then calcined at 900 °C for 3 h in air or helium atmosphere. The particles of -22 to -30 mesh sizes were prepared from the calcined solid mass of the samples of the calcium zirconate.

2.5. Preparation of samples of the calcium zirconate by template method

The different samples of the calcium zirconate with different moles ratios of Ca/Zr = 0.5,1, 2, 3, 4 and 6 were prepared by using CTAB (Cetyl tri methyl ammonium bromide) as a template. The samples of the calcium zirconate with Ca/Zr = 1 mol ratio were prepared as follows. The solution A was prepared by dissolving 0.00611 mol of CATB in 1.09 mol of distilled water by addition of 0.0133 mol of NaOH in 0.34 mol of water. Then solution A was stirred for 1 h for getting clear homogeneous solution. The solution B was prepared by mixing 0.0115 mol of zirconium (IV) propoxide and 0.0015 mol of TMAOH (tetra methyl ammonium hydroxide) in 2.78 mol of water by constant stirring. Then, solution A was added into the solution B by stirring. In the mixture of solutions, 0.027 mol of $CaCO_3$ was added as calcium precursor. The solution mixture was aged for 24 h in order to complete the precipitation. Then, the solid mass was separated by filtration from the solution mixture. The separated solid mass was washed with distilled water in order to remove the dissolved and unwanted material. Further, the solid mass was dried in an oven at 100 ^{0}C for 6 h. Then, the dried mass was calcined in a furnace in air at 900 ^{0}C for 3 h. The particles of -22 to -30 mesh sizes were prepared from the calcined solid mass. The different samples of the calcium zirconate with different moles ratios of Ca/Zr were prepared by varying the quantity of zirconium (IV) propoxide. However, the mol ratio of Ca/Zr in the calcined mass of the samples of the calcium zirconate was determined by EDAX analysis for the Ca/Zr mol ratio confirmation.

2.6. Preparation of samples of the calcium zirconate by micro emulsion method

The some samples of the calcium zirconate of different Ca/Zr = 0.5, 1, 2, 3, 4 and 6 moles ratios were prepared by using micro emulsion method. The solution A was prepared by stirring and adding the 0.61 mol of cyclohexane as the oil phase, 0.035 mol of Triton X – 100 as surfactant, 0.107 mol of *n*-hexanol as co-surfactant in 0.035 mol of water. Solution B was prepared by adding and stirring the zirconium (IV) propoxide and calcium hydroxide in 0.5 M ammonium hydroxide. For the preparation of samples of the calcium zirconate of Ca/Zr = 1 mol ratio, 0.04 mol each of calcium hydroxide and zirconium (IV) propoxide were used. The solution A and B were slowly mixed together with constant stirring. After aging this reaction mixture for two hours, the precipitated solid mass was separated by centrifugation. The solid mass was washed with acetone and then solid mass was dried in an oven at 110 ^{0}C for 10-12 h. The dried solid mass was calcined in a furnace in the air at 900 ^{0}C for 3 h. However, for the preparation of samples of the calcium zirconate of different Ca/Zr mol ratios, zirconium (IV) propoxide moles were varied. The particles of -22 to -30 mesh sizes were prepared from the calcined solid mass of the sample of the calcium zirconate.

2.7. Procedure for CO_2 adsorption by the samples of the calcium zirconate

The procedure for carbon dioxide adsorption was evolved with the designed set up with the gaseous connections. The gaseous connection set up was designed by using 4 mm od stainless steel tubing, four three ways valves, gas sampling valve, carbolite split furnace with temperature controller, a quartz reactor, Nucon GC and flow control valves as described in the Figure 1. During the adsorption process of CO_2, the flows of helium and carbon dioxide were changed with four three way valves as needed for the flushing and adsorption. A quartz tube reactor was fabricated from a quartz tube with the dimensions of 6 mm od, 4 mm id and 850 mm length. The quartz tube reactor at the centre was designed of the dimensions of 10 to 20 mm id and 100 mm length with a quartz tube. The sample of the adsorbent was placed inside at the center of the quartz tube reactor with the support of quartz wool. The temperature of the bed of the sample of the adsorbent was maintained by setting the quartz reactor inside the split furnace with the gaseous connections. The quartz reactor was connected by stainless tubing and connectors through four three ways valves and a sampling valve to GC. The 0.01 to 0.25 g amount of bed of the sample of the adsorbent with the particle size -22 to -30 meshes was used at the center of the quartz tube reactor for CO_2 adsorption. The temperature of a split furnace with quartz reactor was controlled by a programmed temperature controller. The temperature of the bed of the sample of the adsorbent was recorded by using a

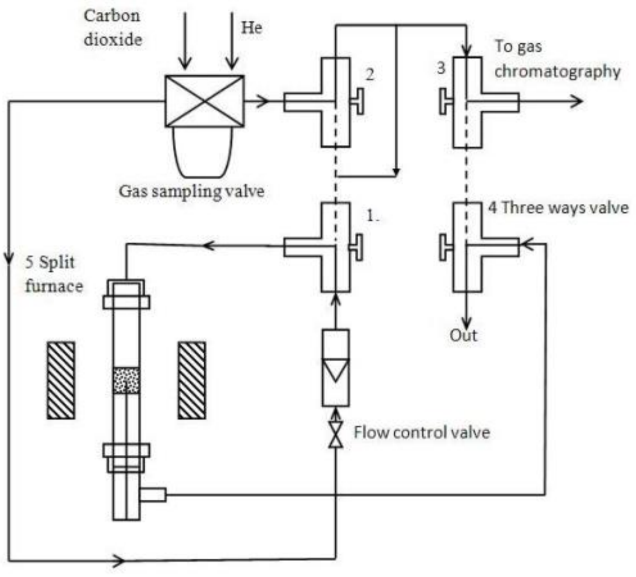

Figure 1. The designed schematic set up for the carbon dioxide adsorption

thermocouple and digital temperature indicator. First, the bed of the sample of the adsorbent was flushed with helium gas in order to remove the stresses of the impurity gases from the bed of the sample of the adsorbent, gaseous connections and quartz reactor. Then, the bed of the sample of the adsorbent was flushed with CO_2 to remove the free helium gas. After that, the carbon dioxide was allowed to adsorb over the bed of the sample of the adsorbent at a certain pressure, temperature and time in the absence of helium gas. The adsorbed carbon dioxide by the bed of the sample of the adsorbent was removed by using the helium as a carrier gas and increasing the temperature of the quartz reactor containing the bed of the sample of the adsorbent. The removed carbon dioxide was estimated by GC using a Porapak-Q column and thermal conductivity detector. The analyzed carbon dioxide was expressed as adsorbed CO_2 in wt% by the sample of the adsorbent of calcium zirconate at STP.

2.8. Characterization of the samples of the calcium zirconate

The samples of the calcium zirconate adsorbent were characterized by the acid-base titrations for alkalinity/acidity, by X-ray diffraction (Philips Power XRD) for XRD patterns, for surface area by surface analyzer (Model Autosorb–1, Make-Quanta chrome Instruments Pvt. LTD, USA) and SEM images (QUANTA 200 3D). The samples of the calcium zirconate prepared by sol gel, solid-solid fusion template and micro emulsion methods were selected for the characterization.

3. Results and Discussion

3.1 Mechanism of CO_2 adsorption by the samples of the calcium zirconate

The CO_2 reacts with the samples of the calcium and zirconium oxide to form the carbonates at higher temperature. The reactions of formation of

$$xCaO + y\,ZrO_2 \leftrightarrow Ca_xZr_yO_{(x+2y)} \qquad (1)$$

$$Ca_xZr_yO_{(x+2y)} + (x+y)\,CO_2 \leftrightarrow xCaCO_3 + y\,ZrOCO_3$$

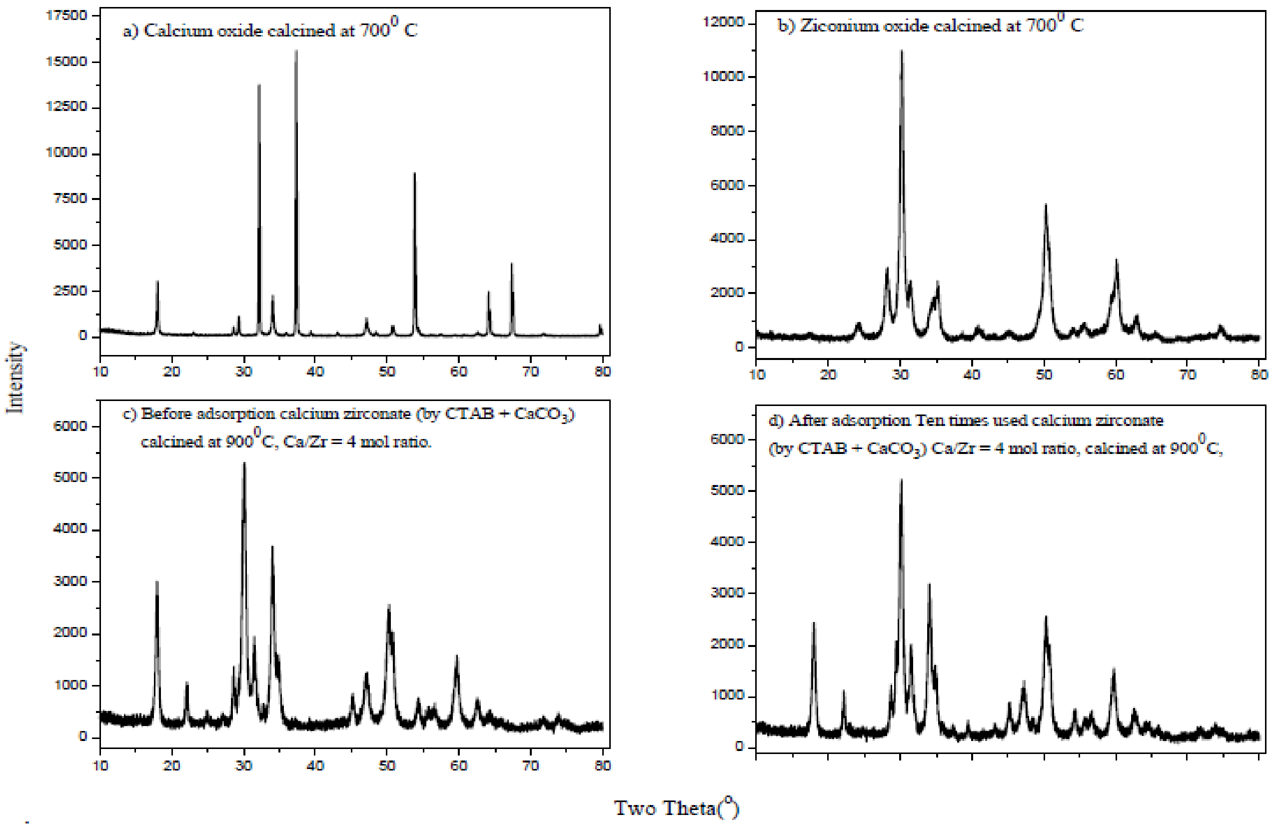

Figure 2. XRD pattern of (a) the sample of the calcium oxide, (b) sample of the zirconium oxide, (c) the sample of the calcium zirconate before the CO_2 adsorption and the sample of the calcium zirconate was prepared by template CTAB + $CaCO_3$ method, (d) the sample of the calcium zirconate after ten times was used to CO_2 adsorption and the sample of the calcium zirconate was prepared by the template CTAB + precursor $CaCO_3$ and calcined at 900 °C for 3 h.

calcium zirconate, calcium and zirconium carbonates are given by the following equations. In which the x and y represent the mol fractions of the calcium and zirconium, respectively. Calcium carbonate is stable however, zirconium carbonate is meta-stable.

3.2. Characterization of the samples of the calcium zirconate

The samples of the calcium zirconate were characterized by using surface area, alkalinity/acidity, SEM images and XRD patterns. In the Figures 2a and 2b, the XRD patterns were shown of the samples of the calcium zirconate before the CO_2 adsorption. Where, the samples of the calcium zirconate were prepared by the solid-solid fusion method by using the calcium and zirconyl nitrates precursors. The samples of the calcium zirconate were calcined at 900 ^{0}C for 3 h. In the XRD patterns of the samples of the calcium zirconate, the calcium oxide, zirconium oxide and calcium zirconate phases were observed. In the Figure 2 (c), the XRD patterns of the samples of the calcium zirconate were shown. In this case, the samples of the calcium zirconate were prepared by using the template CTAB and precursor $CaCO_3$. The samples of the calcium zirconate were used for the CO_2 adsorption and then the XRD patterns of the samples of the calcium zirconate were recorded. The XRD patterns of the samples of the calcium zirconate show the crystalline phases of CaO, ZrO_2 and $CaZrO_3$. The observed XRD patterns of the samples of the calcium zirconate indicate that the calcium zirconate phase was regenerated. In the Figure 2 d, XRD patterns of the samples of the calcium zirconate show the crystalline phases of CaO, ZrO_2 and $CaZrO_3$. Where, the samples of the calcium zirconate were used for CO_2 adsorption for ten times after the CO_2

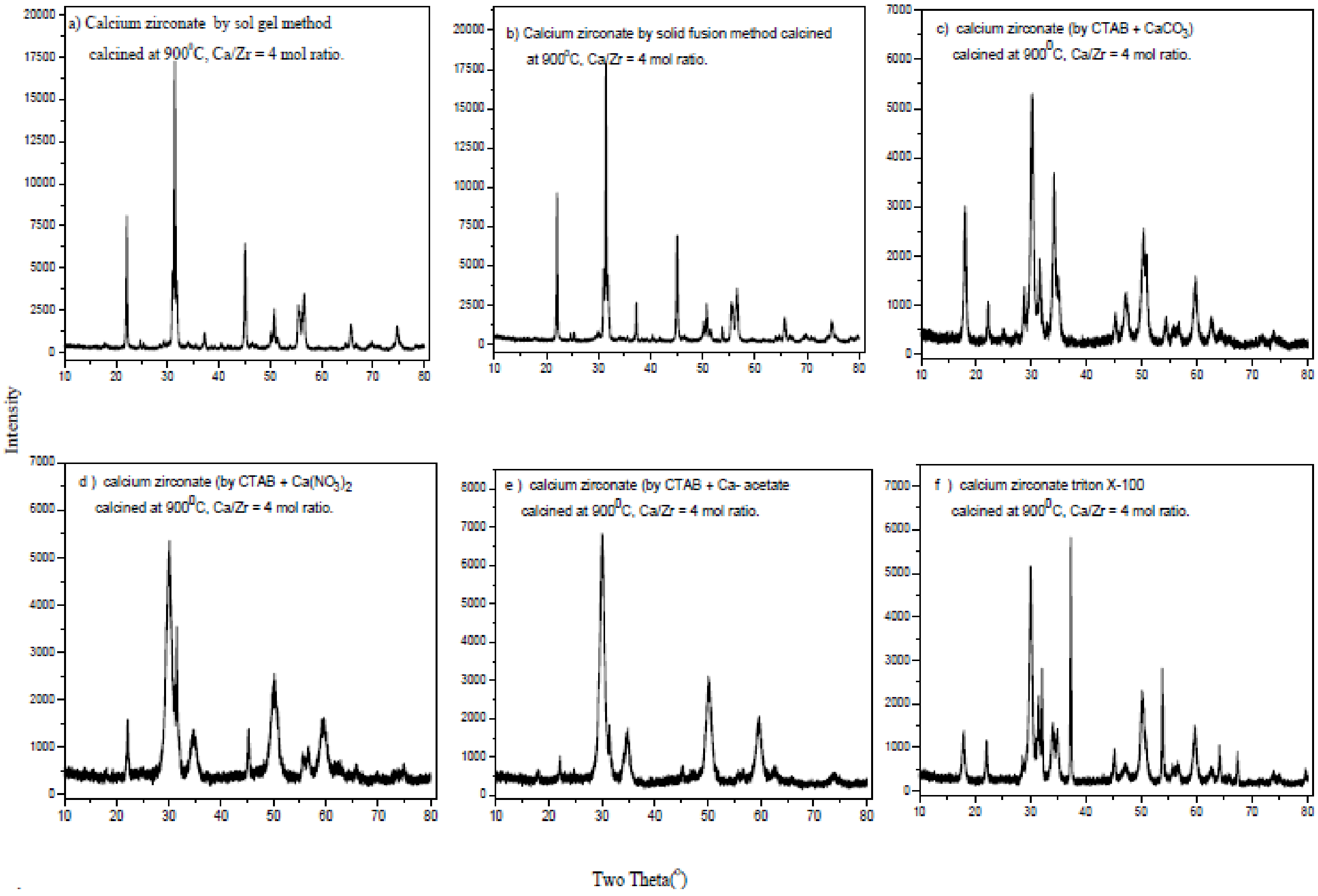

Figure 3. XRD pattern of (a) the sample of the calcium zirconate was prepared by sol gel method, (b) the sample of the calcium zirconate was prepared by solid- solid fusion method, (c) the sample of the calcium zirconate was prepared by CTAB + $CaCO_3$ method, (d) the sample of the calcium zirconate was prepared by template CTAB + $Ca(NO_3)_2$ method, (e) the sample of the calcium zirconate was prepared by template CTAB + Ca - acetate method and (f) the sample of the calcium zirconate was prepared by template triton X – 100 method.

desorption. The results of characterization of the samples of the calcium zirconate by XRD pattern show that the calcium zirconate phase was regenerated during the process of CO_2 adsorption and desorption.

Figure 3 shows the XRD patterns of the samples of the calcium zirconate. In the Figure 3a, the XRD patterns of the samples of the calcium zirconate were shown for the sample of calcium zirconate with Ca/Zr = 4 mol ratio. The samples of the calcium zirconate were prepared by the sol-gel method by using the precursor calcium and zirconyl nitrate and then samples of the calcium zirconate were calcined in air for 3 h at 900 ^{o}C. The $CaZrO_3$ and CaO phases were observed in the samples of the calcium zirconate. In the Figure 3 b, the XRD patterns were shown of the samples of the calcium zirconate with Ca/Zr = 4 mol ratio. The samples of the calcium zirconate were prepared by solid-solid fusion method by using the precursors $CaCO_3$ and zirconyl nitrate and then the samples of the calcium zirconate were calcined in air at 900 ^{o}C for 3 h. In the Figure 3 c, XRD patterns of the samples of the calcium zirconat were shown. The samples of the calcium zirconate were prepared by using the template CTAB and precursor $CaCO_3$. The crystalline phase of CaO was observed at 35^0 in the samples of the calcium zirconate (Figure c). In the Figure 3d and 3e, the XRD patterns of the samples of the calcium zirconate were shown. The samples of the calcium zirconate were prepared by using the template CTAB and precursors $Ca(NO_3)_2$ (Figure 3d) and calcium acetate (Figure 3 e). The CaO phase at 35^o was not observed in the XRD patterns of the samples of the calcium zirconate indicating that the calcium zirconate phase was dominantly formed and observed in the samples of the calcium zirconate.

In the Table 1, the surface areas of the samples of the calcium oxide, zirconium oxide, alumina and silica were given. The samples of the calcium zirconate are very low surface area; however, the CO_2 reactions with the samples of the calcium zirconate are governed by the Equations 1 and 2 which reactions are the calcium and zirconium carbonate formation. Where, the samples of the calcium oxide were prepared by calcining calcium nitrate at 900 ^{0}C for 3 h, the samples of the

Table 1. The surface area, alkalinity/ acidity of the samples of the calcium zirconate, and the CO_2 adsorption by the samples of the calcium zirconate

Sr. No	Calcium zirconate, Ca/Zr mol ratio	Alkalinity, mmol g^{-1}	Surface area, m^2g^{-1}	CO_2 adsorption at 600^0 C, wt %
1	CaO	20.0	9.37	6.88
2	ZrO_2	0.56 (Acidity)	81.97	8.39
3	SiO_2	1.1 (Acidity)	236.39	1.10
4	Al_2O_3	2.4	67.56	12.24
	Sol-gel method			
5	The sample of calcium zirconate (Ca/Zr = 4 mol ratio) calcined in the air 900^0C for the 3h	3	2.25	18
	Solid-solid fusion method			
6	The sample of $CaCO_3$ and $ZrO(NO_3)_2$ (Ca/Si= 4 mol ratio) calcined in the air for the 3h	5		19.61
	Template method			
7	The sample of calcium zirconate with CTAB + NaOH + TMAOH + $CaCO_3$+ $ZrO(NO_3)_2$ (Ca/Zr = 4 mol ratio initial) calcined in the air for the 3 h	11.8	11.84	23.39
8	The sample of calcium zirconate with (CTAB) + NaOH + TMAOH + $Ca(NO_3)_2$ + ZrO $(NO_3)_2$(Ca/Zr = 4 mol ratio initial) calcined in the air for the 3h	1.2	15.35	15.92
9	The sample of calcium zirconate with (CTAB) + NaOH + TMAOH +Calcium acetate +$ZrO(NO_3)_2$ (Ca/Zr = 4 mol ratio initial) calcined in the air for the 3 h	1.5	11.71	17.32
	Micro emulsion method			
10	The sample of calcium zirconate with cyclohexane + Triton X – 100 + *n*-hexanol + calcium hydroxide + zirconium (IV) propoxide (Ca/Si= 4 mol ratio initial) calcined in the air for the 3h	19.6	3.19	24.81

zirconium oxide were prepared by calcining zirconly nitrate at 900 ^{0}C for 3 h, the samples of the fumed silica (Aldrich) were used, and the samples of the alumina were prepared by calcining aluminium hydroxide at 900 ^{0}C for 3 h. The surface areas of the samples of the calcium oxide, zirconium oxide, alumina and silica were 9.37, 81.97, 236.39 and 67.56 m^2 g^{-1}, respectively. The surface areas of the samples of the calcium zirconate prepared by different methods such as sol-gel (by using precursors $Ca(NO_3)_2$ and $ZrO(NO_3)_2$ with Ca/Zr = 4 mol ratio and calcined at 900 ^{o}C for 3 h), solid-solid fusion (by using precursors $CaCO_3$ and $ZrO(NO_3)_2$ of Ca/Zr = 4 mol ratio and calcined at 900 ^{o}C for 3 h), template method (by using precursors CTAB and $ZrO(NO_3)_2$ of Ca/Zr = 4 mol ratio and also using precursors CTAB and calcium acetate of Ca/Zr = 4 mol ratio and calcined at 900 ^{o}C for 3 h), micro emulsion (by using the precursors $Ca(OH)_2$ and $ZrO(NO_3)_2$ and calcined at 900 ^{o}C for 3 h) were observed 2.5, 10.50, 11.84, 15.35, 11.71 and 3.29 m^2 g^{-1}, respectively (Table 1). The observed surface areas of the samples of the calcium zirconate were low. The CO_2 adsorption could be mainly due to the calcium and zirconium carbonate formation in the samples of the calcium zirconate at higher temperature.

In the Figures 4 a-d, the selected SEM images of the samples of the calcium zirconate were given. Where, the samples of the calcium zirconates were prepared by different methods such as sol-gel (by using precursors $Ca(NO_3)_2$ and $ZrO(NO_3)_2$ of Ca/Zr = 4 mol ratio), solid-solid fusion (by using the precursors $CaCO_3$ and $ZrO(NO_3)_2$ of Ca/Zr = 4 mol ratio), template (by using precursors $CaCO_3$, CTAB and $ZrO(NO_3)_2$ of Ca/Zr = 4 mol ratio), and micro emulsion (by using precursors $Ca(HO)_2$ and $ZrO(NO_3)_2$) methods. The SEM images show the

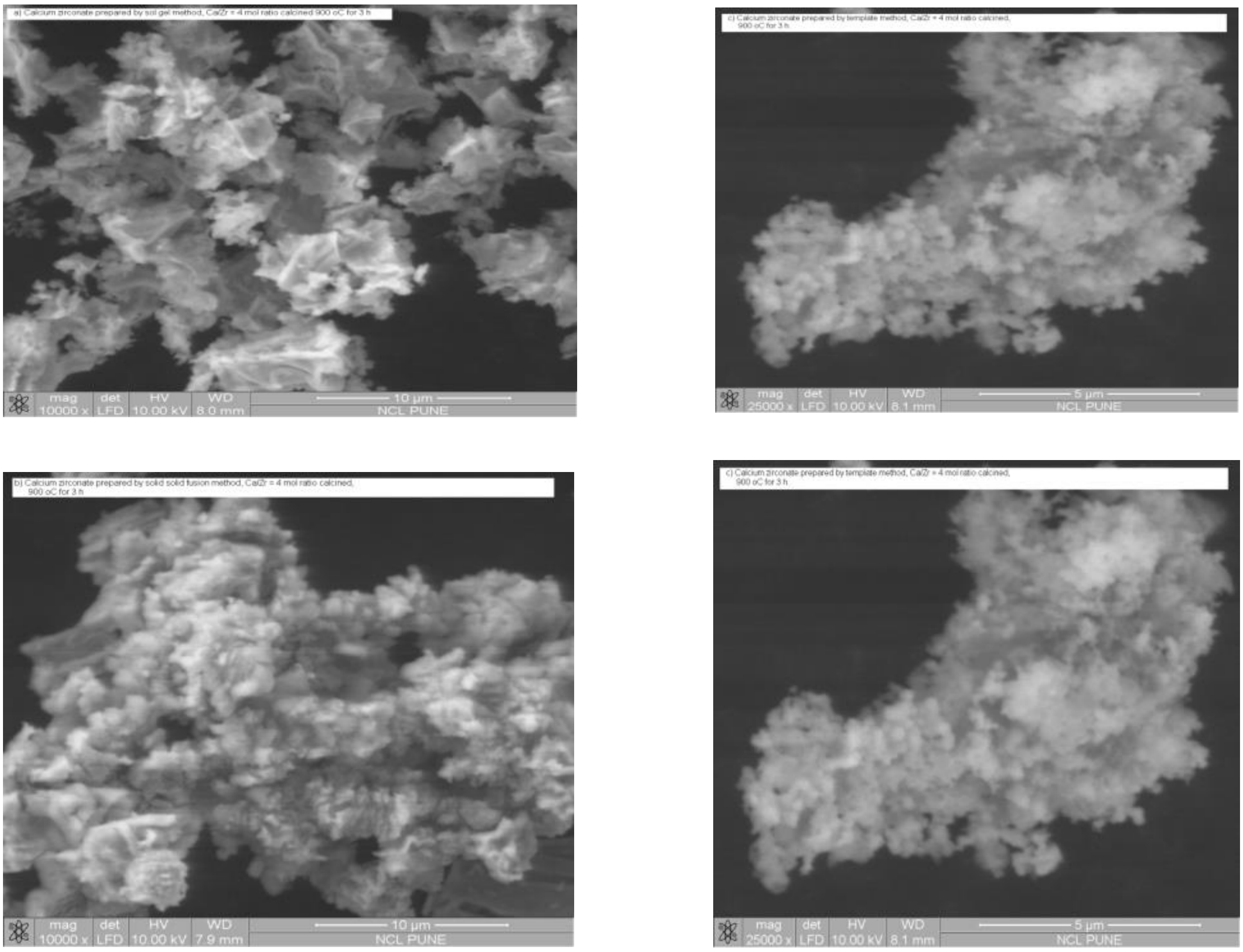

Figure 4. SEM images of (a) the sample of the calcium zirconate was prepared by sol gel method (Ca/Zr= 4 mol ratio) and calcined at 900 ^{o}C for 3 h, (b) the sample of the calcium zirconate was prepared by solid-solid fusion method (Ca/Zr = 4 mol ratio) and calcined at 900 ^{o}C for 3 h, (c) the sample of the calcium zirconate was prepared by template method (Ca/Zr = 4 mol ratio) and calcined at 900 ^{o}C for 3 h and (d) the sample of the calcium zirconate was prepared by micro emulsion method (Ca/Zr = 4 mol ratio) and calcined at 900 ^{o}C for 3 h.

crystalline particles of the calcium zirconate, calcium and zirconium oxides in the samples of calcium zirconate.

3.3. Themo-gravimetric analysis of the samples of calcium zirconate

The thermo-gravimetric analysis was done in order to check the loss in weight and also moisture content in the samples of calcium zirconate (calcined the calcium zirconate at 900 °C for 3 h). In the Figure 5, thermo-gravimetric curve was shown for the samples of calcium zirconate. The samples of calcium zirconate with Ca/Zr = 4 mol ratio were prepared by using the template CTAB and precursor $CaCO_3$. The estimated loss in weight in the samples of the calcium zirconate was 16.97 wt % for the studied temperature range from 40 to 900 °C. The loss in weight in the samples of the calcium zirconate was due to the loss of moisture from the samples of the calcium zirconate. However, the presence of moisture in the samples of the calcium zirconate also helps for the adsorption of CO_2.

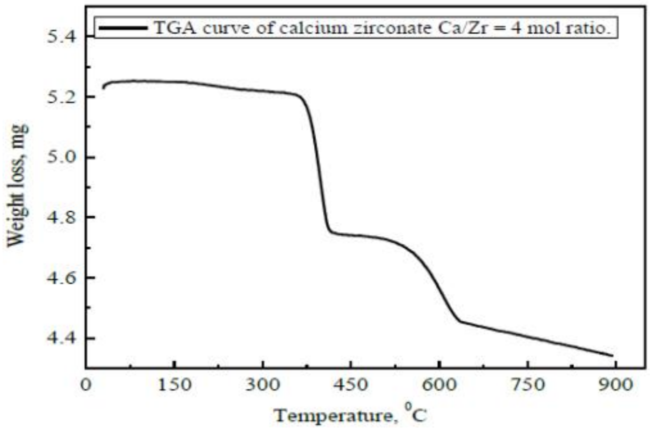

Figure 5. Thermo-gravimetric analysis of the sample of the calcium zirconate of Ca/Zr = 4 mol ratio was prepared by using template CTAB and $CaCO_3$

3.4. Temperature profile of carbon dioxide adsorption by the samples of the calcium zirconate

The CO_2 adsorptions at 600 °C by samples of CaO, ZrO_2, SiO_2 and alumina observed were 6.88, 8.39, 1.1 and 12.24 wt%, respectively, (Table 1). In the Figure 6, the CO_2 adsorption in wt % by the sample of calcium zirconate with Ca/ Zr = 4 mol ratio was shown for the temperature range from 100 to 850 °C. The samples of the calcium zirconate were prepared by the sol gel, solid-solid fusion, template and micro emulsion methods. Then, these samples of calcium zirconate were calcined at 900 °C in air for 3 h. The CO_2 adsorption in wt% by sample of calcium zirconate was observed in two major temperature chromatogram zones from 100 to 400 °C and 400 to 850 °C. The first 100 to 400 °C temperature chromatogram zone of CO_2 adsorption by sample of calcium zirconate was shown the CO_2 adsorption 7 to 17 wt%. This first 100 to 400 °C temperature chromatogram zone represents the post-combustion temperature. However, the second 400 to 850 °C temperature chromatogram zone of CO_2 adsorption by sample of calcium zirconate was shown the CO_2 adsorption in the range 15 to 25 wt %. This second 400 to 850 °C temperature chromatogram zone represents the pre-combustion temperature. The CO_2 adsorption by the sample of calcium zirconate was highest at 600 °C. The CO_2 adsorption by the sample of calcium zirconate prepared by sol gel method with Ca/Zr = 4 mol ratio and calcined in helium at 900 °C was shown 18 wt% at 600 °C. However, the CO_2 adsorptions at 600 °C by the samples of calcium zirconate were 19.61, 23.39 and 24.84 wt%, respectively, when the sample of calcium zirconate with Ca/Zr = 4 mol ratio were prepared by different methods such as solid-solid fusion, template and micro emulsion methods. Then, these samples of calcium zirconates were calcined in air at 900 °C for 3h. The CO_2 adsorption at 600 °C by the sample of calcium zirconate was higher than that of the CO_2 adsorption by the samples of CaO and ZrO_2.

3.5. CO_2 adsorption at 600 °C by the samples of calcium zirconate (sol-gel method)

In order to assess the role of Ca/Zr mol ratio in

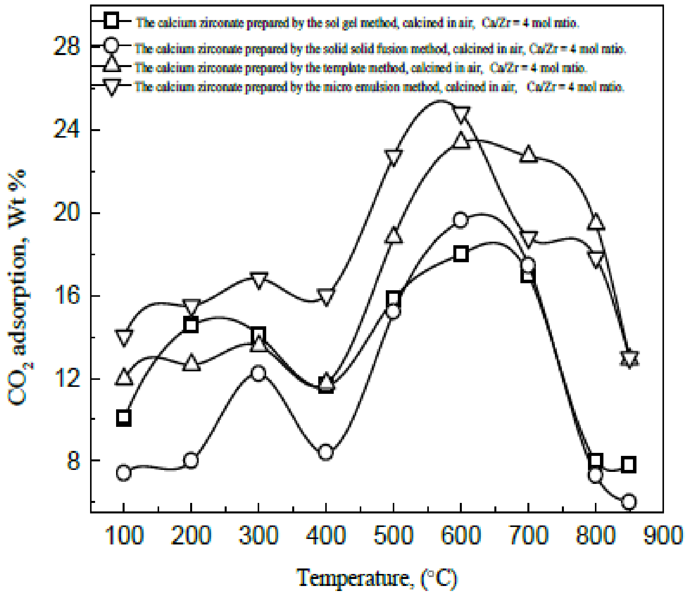

Figure 6. Temperature profile of the carbon dioxide adsorption by the sample of the calcium zirconate where the samples of the calcium zirconate were prepared by different methods.

the CO_2 adsorption by the sample of calcium zirconate at 600 °C, the several samples of calcium zirconate with Ca/Zr = 0.5 to 6 mol ratios were prepared by the sol-gel method (Figure 7). Then, these samples of calcium zirconate were calcined at 900 °C for 3 h in air. The alkalinity of the samples of calcium zirconate and CO_2 adsorption by the samples of calcium zirconate with Ca/Zr = 0.5 to 6 mol ratios were observed in the range from 0.2 to 9.4 mmol g^{-1} and 10.22 to 23.86 wt%, respectively. The results indicate that the CO_2 adsorption by the samples of calcium zirconate and alkalinity of samples of the calcium zirconate were increased with the increased in the mol ratio of Ca/Zr in the samples of the calcium zirconate.

3.6. CO_2 adsorption at 600 °C by the sample of calcium zirconate (solid-solid fusion method)

In the Figure 8, the alkalinity of the samples of calcium zirconate with Ca/Zr = 0.5 to 6 mol ratio and CO_2 adsorption by the samples of calcium zirconate with Ca/Zr = 0.5 to 6 mol ratio at 600 °C were shown. The alkalinity of samples of the calcium zirconate and CO_2 adsorption by the samples of calcium zirconate with Ca/Zr = 0.5 to 6 mol ratio were in the range from 0.06 to 8.4 mmol g^{-1} and 11.12 to 23.32 wt%, respectively. The alkalinity of the samples of the calcium zirconate and CO_2 adsorptions by the samples of the calcium zirconate at 600 °C were increased with the increased in the mol ratio of Ca/Zr (0.5 to 6) in the samples of calcium zirconate.

3.7 CO_2 adsorption at 600 °C by the samples of the calcium zirconate (template method)

The alkalinities of the samples of the calcium zirconate and CO_2 adsorption by the samples of the calcium zirconate were 11.8, 1.5 and 1.2 mmol g^{-1} and 23.39, 17.32 and 15.92 wt %, respectively (Figure 9). Where, the samples of the calcium zirconate were prepared by using of the template CTAB and the precursors $CaCO_3$, Ca $(NO_3)_2$ and calcium acetate. In the process of preparation of samples of the calcium zirconate with Ca/Zr = 0.5 to 6 mol ratios by using the template CTAB and precursors $Ca(NO_3)_2$, $CaCO_3$ and calcium acetate, the $Ca(NO_3)_2$ and calcium acetate were relatively more soluble in aqueous solution in comparison with that of $CaCO_3$. The results indicated that the alkalinity of the samples of the calcium zirconate and CO_2 adsorption by the samples of the calcium zirconate at 600 °C was increased with the increased in the mol ratio of Ca/Zr from 0.5 to 6 in the samples of calcium zirconate.

3.8 CO_2 adsorption at 600 °C by the samples of the calcium zirconate (micro emulsion method)

In the Figure 10, the alkalinity of the samples of the calcium zirconate and CO_2 adsorption by the samples of the calcium zirconate at 600 °C with

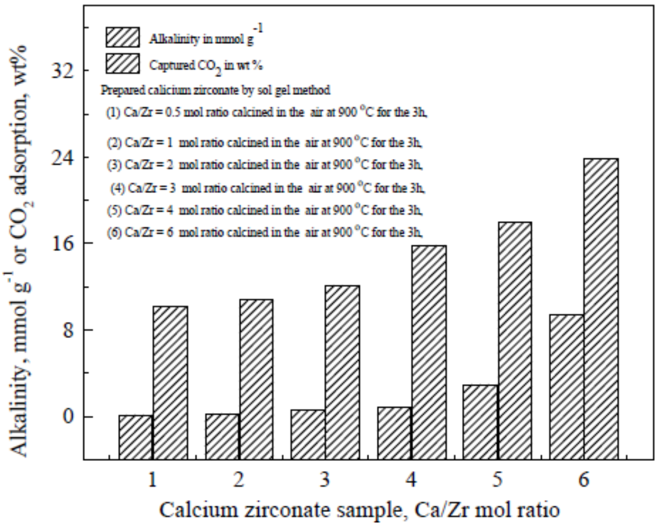

Figure 7. The plot of alkalinity of the samples of the calcium zirconate and CO_2 adsorption by the samples of the calcium zirconate against the different Ca/Zr mol ratios of the samples of the calcium zirconate where the samples of the calcium zirconate were prepared by the sol-gel method.

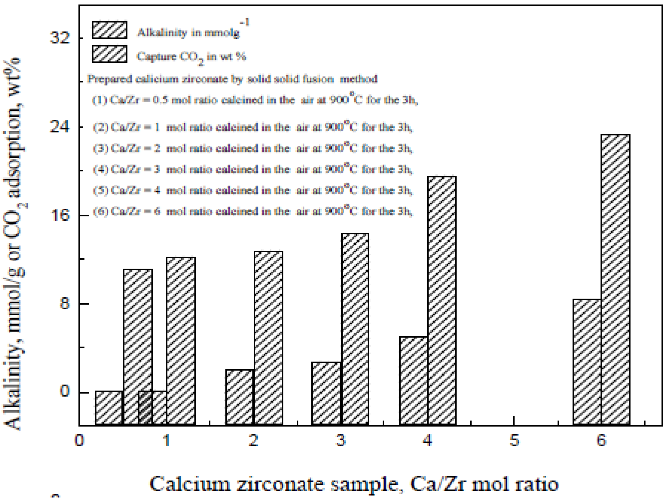

Figure 8. The plot of alkalinity of the samples of the calcium zirconate and CO_2 adsorption by the samples of the calcium zirconate against the different Ca/Zr mol ratios of the samples of the calcium zirconate where the samples of the calcium zirconate were prepared by the solid-solid fusion method.

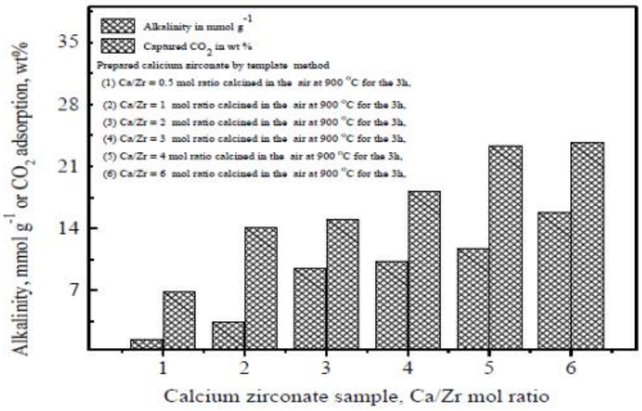

Figure 9. The plot of alkalinity of the samples of the calcium zirconate and CO_2 adsorption by the samples of the calcium zirconate against the different Ca/Zr mol ratios of the samples of the calcium zirconate where the samples of the calcium zirconate were prepared by the template method.

Ca/Zr = 0.5 to 6 mol ratio were presented. The observed alkalinity of the samples of the calcium zirconate with Ca/Zr = 0.5 to 6 mol ratio was in the range from 1.6 to 23.0 mmol g^{-1}. However, the CO_2 adsorption at 600 °C by the samples of the calcium zirconate with Ca/Zr = 0.5 to 6 mol ratio was in the range from 12.1 to 27.01 wt %. The results indicated that the alkalinities of the samples of the calcium zirconate and CO_2 adsorption by the samples of the calcium zirconate were increased along with the increased in the Ca/Zr mol ratio from 0.5 to 6 in the samples of the calcium zirconate.

The acidity/alkalinity of the samples of the calcium zirconate depends on the mol ratio of the Ca/Zr in the samples of the calcium zirconate. The estimated alkalinity (Table 1) of the samples of the CaO, acidity of the samples of the SiO_2 and ZrO_2 were 20, 1.1 and 0.56 mmol g^{-1}, respectively. However, the CO_2 adsorption by the samples of the CaO, SiO_2 and ZrO_2 were 6.88, 1.1 and 8.39 wt %, respectively. The CO_2 adsorption by the samples of the CaO, SiO_2 and ZrO_2 at 600 °C was in the agreement with the alkalinity and acidity of the samples of the CaO, SiO_2 and ZrO_2. Moreover, the alkalinities of the samples of the calcium zirconate and CO_2 adsorption by the samples of the calcium zirconate were in the order of increased Ca/Zr mol ratio from 0.5 to 6 of in the samples of the calcium zirconate (Figures 7-10).

3.9. Effect of promoters on CO_2 adsorption

To check the effect of promoters on the CO_2 adsorption by the samples of the calcium zirconate at pre-combustion temperature, 2 wt % loadings of alkali metals (K^+, Na^+, Rb^+, Cs^+, etc.), lanthanide metal (La^{3+}), transition metal (Ag^+) were done over the samples of the calcium zirconate. The promoted samples of the calcium zirconate were calcined at 900 °C for 3h. Table 2 shows the alkalinity of the samples of the calcium zirconate and CO_2 adsorption by the promoted samples of the calcium zirconate. The CO_2 adsorption by the promoted samples of the calcium zirconate by alkali metals showed the trend in the increased order of Na < K < Cs < Rb. However, the promoter effects of Ag and La for the CO_2 adsorption by the samples of the calcium zirconate were lower in comparison with that of the alkali metals promoted samples of the calcium zirconate.

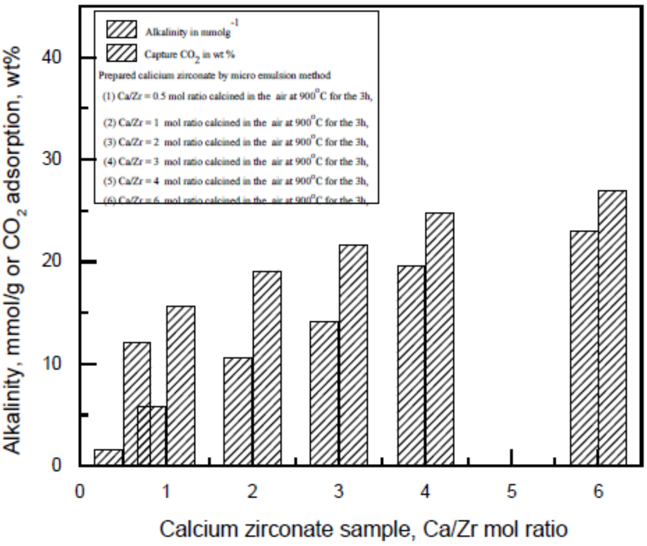

Figure 10. The plot of alkalinity of the samples of the calcium zirconate and CO_2 adsorption by the samples of the calcium zirconate against the different Ca/Zr mol ratio of the samples of the calcium zirconate where the samples of the calcium zirconate were prepared by micro emulsion method.

3.10. The effect of exposure time on the adsorption of CO_2 by the sample of the calcium zirconate

The sample of the calcium zirconate was prepared by the solid-solid fusion method by using the calcium carbonate and zirconyl nitrate. The sample of the calcium zirconate was calcined at 900 °C in helium atmosphere for 3 h. In the Figure 11, the effect of exposure time of CO_2 over the sample of the calcium zirconate for the CO_2 adsorption was presented for the time until 120 min. The CO_2 adsorption by the sample of the calcium zirconate was observed for the above period 40.5 wt %.

3.11. The regenerability of calcium zirconate sample

The regenerability of the sample of the calcium zirconate for CO_2 adsorption was tested (Figure 12). The used sample of the calcium zirconate was prepared by the micro emulsion method and calcined in air with Ca/Zr = 4 mol ratio. The CO_2 adsorption and de-sorption by the sample of calcium zirconate are the reactions of the formation of metal carbonate and decomposition of metal carbonate at higher temperature > 450 °C, respectively. The metal carbonate formation is a solid-gas reaction between the metal oxide and CO_2 gas. However, the metal carbonate decomposition (solid to gas and solid) is a solid reaction of formation of metal oxide and CO_2. In addition to this, the solid-solid calcium oxide and zirconium oxides also react to each other to generate the solid crystalline phase of calcium zirconate. Simultaneously, the three reactions parallel and continuously competitively occurring are the formation of calcium and zirconium carbonate, decomposition of calcium and zirconium carbonate and calcium zirconate crystalline phase reformation from calcium and zirconium mixed oxide. However, one of the reactions is certainly dominating at a certain temperature > 450 °C. In order to check the regenerability of the sample of the calcium zirconate, a sample of the calcium zirconate was tested for 50 cycles at certain temperature repeatedly for the adsorption and desorption of CO_2 at high and low temperatures. However, there was no change in the capacity of the sample of the calcium zirconate for adsorption and de-sorption of CO_2 (Figure 12).

Table 2. The alkalinity of the promoted the sample of calcium zirconate and the CO_2 adsorption at 600^0 C by the promoted the sample of calcium zirconate with Ca/Zr = 4 mol ratio (the promoted the samples of calcium zirconate were prepared by solid-solid fusion method)

Sr. No	Metal loaded, 2 Wt %	Alkalinity, $mmol^{-1}$	CO_2 adsorption, wt %
1		5.0	19.61
2	Na	5.4	24.74
3	K	5.6	25.83
4	Rb	7	29.53
5	Cs	9.6	31.19
6	La	5.2	24.46
7	Ag	4.0	23.82

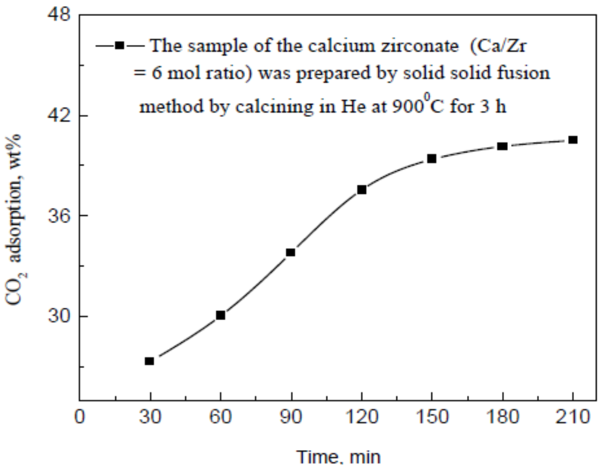

Figure 11. The effect of exposure time of CO_2 over the samples of the calcium zirconate on the CO_2 adsorption by the samples of the calcium zirconate.

4. Conclusion

The several samples of the calcium zirconate were prepared by different methods such as sol gel, solid-solid fusion, template and micro-emulsion methods. The samples of the calcium zirconate were prepared by template and micro emulsion methods showed the higher CO_2 adsorptions in comparison with that of the samples of the calcium zirconate were prepared by other methods. The increased alkalinities of the samples of the calcium zirconate and CO_2 adsorption by the samples of the calcium zirconate were observed in the increased order of the mol ratio of Ca/Zr from 0.5 to 6 in the samples of the calcium zirconate. The thermo gravimetric analysis of the samples of the calcium zirconate showed that the samples of the calcium zirconate adsorb the moisture which was the cause

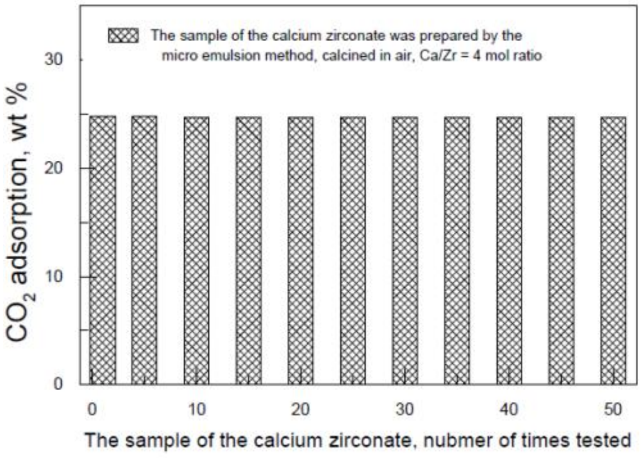

Figure 12 Regenerability of calcium zirconate, the sample of the calcium zirconate was prepared by the micro emulsion method and calcined in air with Ca/Zr = 4 mol ratio

of loss in weight of the samples of the calcium zirconate. However, moisture in the samples of the calcium zirconate helps for the CO_2 adsorption. The promoters like K^+, Na^+, Rb^+, Cs^+, Ag^+ and La^{3+} showed the increased CO_2 adsorption by the samples of the calcium zirconate. The exposure time of CO_2 on the CO_2 adsorption by the samples of the calcium zirconate is also an important parameter. The regenerable and reusable samples of the calcium zirconate were found to be for the adsorption of CO_2 at the post- and pre-combustion temperatures.

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