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Research Article

The Applications of Mixed Metal Oxides to Capture the CO_2 and Convert to Syn-Gas

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Abstract

The applications of different mixed metal oxides were explored for the capture of CO_2 and convert of CO_2 to syn-gas. The several samples of the mixed metal oxides were prepared by the sol-gel, solid-solid fusion, precipitation, molten salt and template methods in order to investigate the performance of mixed metal oxides to the CO_2 applications. These samples were calcined for the 3 h in air at 900 ^oC. The mixed metal oxides samples were characterized by acidity/basicity, surface area, XRD pattern, SEM images and to capture CO_2. The basicity and surface area of the samples of mixed metal oxides were found to be in the range from 0.7 to 15.7 $mmol.g^{-1}$ and 2.24 to 138.76 $m^2.g^{-1}$, respectively. The obtained results of prepared mixed metal oxides by different method were compared for the purpose of searching the efficient materials. The temperature profiles of the captured CO_2 by the samples of mixed metal oxides were obtained in the range 100 to 800 ^oC. The captured CO_2 was found to be in the range from 7.36 to 26.93 wt.%. The conversions of CO_2 by methane were explored to syn-gas over the mixed metal oxides including the calcium iron lanthanum mixed metal oxides and (5 wt.%) Pd/Al_2O_3 at 700 ^oC with the gas hourly space velocities (GHSV) 6000 $ml.h^{-1}.g^{-1}$ of methane, 6000 $ml.h^{-1}.g^{-1}$ of CO_2 and 24000 $ml.h^{-1}.g^{-1}$ of helium.

Keywords: Sol-gel method; capture of CO_2; mixed metal oxides; solid-solid fusion method; syn-gas

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1. Introduction

The lithium, sodium, magnesium and calcium containing mixed metal oxides of aluminates, silicate and zirconate had been explored to capture the CO_2 at different temperature ranges. However, the important concept is how to utilize the captured CO_2 for the conversion into value added products. Due to high thermal stability and low activity of CO_2, the quantitatively conversion of CO_2 to value added product is remained a challenging task. However, the both aspects capture and conversion of CO_2 are important in practical point of view. For these purposes, the amine, mixed metal oxides and their combinations could be useful material. Among the important aspects include the capture the CO_2 and then convert into fuel or hydrocarbons via syn-gas.

The CO_2 capture by the carbon, amine, grafted amines on metallic oxide porous materials, amine supported metallic oxide and non-metallic oxide porous materials, carbon supported on porous metallic oxide or non-metallic oxide materials, porous metallic organic frame had been reported. However, the capture of car-

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bon dioxide will not serve the purpose because these applications will create large storage and volume problems. These porous materials have no capacity of CO_2 conversion to value added products. These materials are thermally unstable at higher temperature > 150 ^oC. The several long chain or short chain amines have been used to capture or separate the CO_2 from the CO_2 containing gaseous mixtures. Due to these drawbacks of these materials, it warrants to use the mixed oxides to capture CO_2 and then convert CO_2 to value added products. The process of captured CO_2 by the mixed metal oxides at higher temperature involved the carbonate formation, adsorption in the pores and on the surface. The mixed metal oxides are thermally stable at post-and pre-combustion temperatures. The CO_2 captured by the carbonate formation by mixed metal oxides is an environmentally reversible and non-polluting process [1-2].

Mainly, magnesium, calcium and lithium aluminates, zirconate or silicate have been explored for the capture of CO_2. The transition metal oxides have also been investigated for the capture of CO_2 [3-5]. The preparation, characterization and properties of lithium containing mixed metal oxides had been reported [2-7]. The different mixed metal oxides were used to capture the CO_2 [7-15]. The catalytically conversion of CO_2 and CH_4 to syn-gas has been reported [16-26]. However, such studies on the multi component mixed metal oxides such as calcium copper titanate, lithium zirconium silicate, calcium copper lanthanide, calcium zirconium silicate, etc. are lacking. Therefore, this paper reported the preparation and characterization of mixed metal oxides by different methods and techniques, respectively, and the applications of mixed metal oxides to capture CO_2 and then conversion to syn-gas.

2. Materials and Methods

The chemicals oxide, carbonate, nitrate and hydroxides of calcium, copper, iron and aluminum were used. The titanium propoxide, butoxide, tetraethyl ortho-silicate, fumed SiO_2 (Sigma-Aldrich), were used for preparation of the samples of the mixed metal oxides. However, the all chemicals used were analytical grade. The high purity gases carbon dioxide and helium were used (Deluxe India Ltd). A high temperature furnace was used to calcine the samples of the mixed metal oxides (Thermax Co. Ltd). A split furnace (Carbolite USA) was used to carry the reaction of carbon dioxide with the samples of the mixed metal oxides at different temperatures. The GC (Nucon India Ltd) with thermal conductivity detector was used to analyze the carbon dioxide.

2.1. Preparation of the Samples of Mixed Metal Oxides

The several samples of the mixed metal oxides were prepared by different methods such as sol gel, precipitation, template, molten salt and solid-solid fusion methods. However, the preparation of the mixed metal oxides of calcium zirconium silicate is given in the details.

2.1.1. Sol-gel method

The different mixed metal oxides were prepared by sol gel method. First, the sol-gel was prepared and dried in vacuum oven. The dried sol-gel mass was calcined in furnace at 900 ^oC for 3 h. For the preparation of calcium zirconium silicate by sol-gel method, zirconium oxy nitrate, calcium nitrate tetra hydrate and tetraethyl ortho-silicate (TEOS) from Sigma Aldrich were used. The TEOS was mixed with ethanol and nitric acid in the mol ratio as TEOS:ethanol:nitric acid, 1:8:0.16 and then hydrolyzed for 45 minutes under stirring conditions. Then, the zirconium oxy and calcium nitrates were added into the mixture (in the mol ratio as Ca:Zr:Si ; 1:1:1, 2:1:1, 4:1:1, and 6:1:1), respectively. The reaction mixture was stirred for 5 h at room temperature. After that the reaction mixture was kept under 60 ^oC for 24 h and then the formed sol was dried at 100 ^oC for 48 h. The dry gel was calcined at 900 ^oC for 3 h. The different mixed metal oxides were also prepared by sol gel method.

2.1.2. Template method

The samples of the calcium zirconium silicate were prepared by the template method by using cetyl trimethyl ammoniumbromide (CTAB) 0.0014 mol, tetra methyl ammonium hydroxide (TMAH) 0.0016 mol, calcium nitrate 0.04 mol (variable 0.08, 0.16 and 0.24 mol), zirconyl nitrate 0.04 mol, tetra ethyl orthosilicate 0.04 mol, sodium hydroxide 0.0245 mol and water 6 mol. The templates CTAB and TMAH were prepared in the aqueous sodium hydroxide solution. Then, tetra ethyl ortosilicate, calcium and zirconyl nitrate solutions drop by drop by using burette were added simultaneously to the template solutions. The reaction mixture was stirred for 24 h. The solid mass was separated by filtration and then dried in a vacuum oven at 100 ^oC for 12 h. The dried mass was calcined at 900 ^oC for 3 h.

2.1.3. Precipitation method

The samples of the calcium zirconium silicate were prepared by the precipitation method by using calcium nitrate 0.04 mol (variable of 0.08, 0.16 and 0.24 mol), zirconyl nitrate 0.04 mol, tetraethyl orthosilicate 0.04 mol, ammonium hydroxide 0.4 to 0.6 mol, and ammonium carbonate 0.3 to 0.5 mol in the aqueous solution.

2.1.4. Molten salt method

The samples of calcium zirconium silicate were prepared by the molten salt method by using calcium nitrate 0.04 mol (variable of 0.08, 0.16 and 0.24 mol), zirconyl nitrate 0.04 mol, SiO_2 0.04 mol and KCl 0.01 mol by drying at 100 ^oC and then calcining at 900 ^oC for 3 h.

2.1.5. Solid-solid fusion method

The samples of the calcium zirconium silicate were prepared by solid-solid fusion method for the different Ca:Zr:Si mol ratios. While preparing the samples of the calcium zirconium silicate with Ca:Zr:Si (6:1:1) mol ratio, 0.072 mol of calcium oxide or carbonate, 0.012 mol of each zirconium carbonate and fumed SiO_2 were used. The solid mass was thoroughly mixed and then calcined at 900 ^oC for 3 h. The both molten salt and solid-solid fusion methods are similar in nature only differ in the use of molten salt. The particles -22 to -30 mesh sizes used for the CO_2 reaction were prepared from the calcined solid mass. Similarly, the samples of calcium copper titanate, calcium iron lanthanide, calcium aluminum silicate and magnesium nickel silicate were prepared by varying the metal mol ratio and by different methods such as solid-solid fusion, precipitation, template, sol-gel and molten salt. The samples of the mixed metal oxides such as calcium zirconium silicate henceforth are quoted by the terminology by taking the first letter of name of metal element, and the metal mol ratio and the method of preparation (sol-gel = G, solid-solid fusion = F, precipitation method = P, molten salt method = M and template method =T), such as, CZSF 111 for Ca:Zr:Si (1:1:1), CZSF311 for Ca:Zr:Si (3:1:1), CZSF4-1 for Ca:Zr:Si (4:1:1) and CZSF611 for Ca:Zr:Si (6:1:1); for calcium copper titanate, CCTF111, CCTF211, CCTF411 and CCTF611, for calcium iron lanthanide, CILF111, CILF211, CILF411, CILF611, calcium aluminium silicate, CASF111, CASF211, CASF411, CASF611, for magnesium nickel silicate, MNSF111, MNSF211, MNSF411and MNSF611.

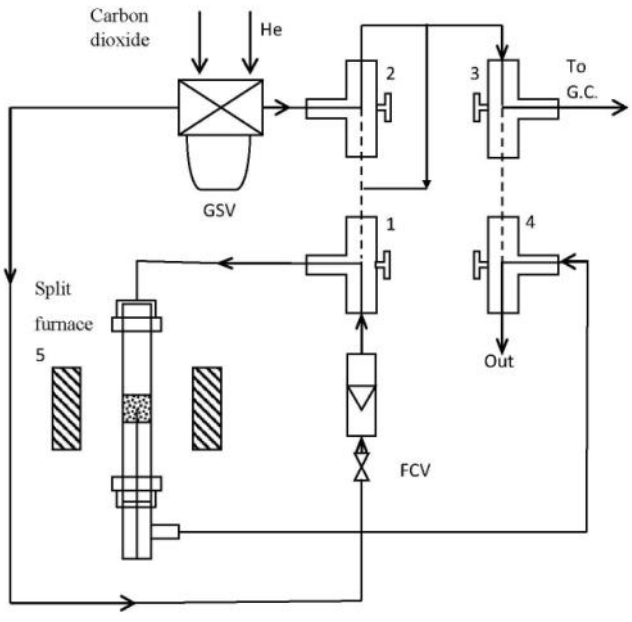

Figure 1. The schematic presentation of CO_2 capture and conversion to syn-gas

2.2. Characterizations of the samples of Mixed Metal Oxides

The samples of the mixed metal oxides were characterized for the basicity/acidity, XRD patterns (Philips Power XRD), NMR, the surface area (Model Autosorb-1, Make-Quantachrome Instruments Pvt. LTD, USA) and SEM images (QUANTA 200 3D).

2.3. Procedure for CO_2 Capture

An online set up of gaseous connection was used (Figure 1) for the capture of carbon dioxide by the samples of mixed metal oxides. The set up was developed by using 4 mm od stainless steel tubing, four three ways gas valves, gas sampling valve, Carbolite split furnace with temperature controller, a quartz reactor, Nucon GC and gas flow control valves. The flow rates of helium and carbon dioxide gases were changed with four three way gas valves as required as shown in the Figure 1. A quartz tube reactor was prepared by using a quartz tube of the dimensions 6 mm od, 4 mm id and 850 mm length. The quartz tube reactor was modified at the centre by using a quartz tube of the dimensions of 10 to 20 mm ID and 100 mm length. The sample of the mixed metal oxides was placed inside and at the center of a quartz tube reactor with the support of quartz wool. The quartz reactor was placed inside a split furnace. The temperature of a split furnace was controlled by a temperature controller. The temperature of the sample of the

mixed metal oxides was measured by using a thermocouple and temperature indicator. The quartz reactor was connected through four three ways gas valves and a gas sampling valve to GC by using stainless steel tubing connections. 0.05 to 0.1 g of the sample of the mixed metal oxides with the particle size -22 to -30 meshes was used to react with CO_2. First, the sample of the mixed metal oxides was flushed with helium gas in order to remove the stresses of other gases. Then, the sample of the mixed metal oxides bed was flushed with CO_2 to remove the free helium gas. After that, the carbon dioxide was allowed to capture by the sample of the mixed metal oxides in absence of helium at a certain pressure, temperature and time. Then, the captured carbon dioxide by the sample of the mixed metal oxides was removed by using helium as a carrier gas, and increasing the temperature of the sample of the mixed metal oxides bed to 900 ^oC. The removed carbon dioxide was analyzed by GC using a Porapak-Q column, thermal conductivity detector (TCD), helium as carrier gas, TCD temperature 100 ^oC, injector temperature 100 ^oC and oven temperature 40 ^oC. The captured carbon dioxide by the sample of the mixed metal oxides was expressed as wt.% of CO_2 at STP. There were two peaks observed [2]. The first peak represented the physic-sorption of weakly bond CO_2. The second peak represented the chemisorptions of strongly bound CO_2.

2.4. Procedure for Conversion of CO_2 to Syn-gas

The conversion of carbon dioxide by methane was carried in the fixed bed quartz reactor (Figure 1). But the system was used by changing the ways of gas through the tree ways gas valves. The temperature of catalyst bed of mixed metal oxides and alumina supported palladium in the fixed bed reactor with helium as carrier gas was controlled at a particular temperature (at 700 ^oC) with temperature controller. Then, a reaction gas mixture was passed through the helium carrier gas through the catalyst bed. The outlet gas mixture was analyzed by pulse method by using gas sampling valve connected to on line system to GC equipped with by using a Porapak-Q column, helium as carrier gas, thermal conductivity detector (TCD), TCD temperature 100 ^oC, FID temperature 100 ^oC, injector temperature 100 ^oC and oven temperature 40 ^oC TCD and FID detectors. The results reported here were of conversion of CO_2 and methane and the selectivity to CO.

3. Results and Discussion

The CO_2 captured by carbonate formation could be given by following equations:

$$CaZrO_3 + CO_2 \leftrightarrow ZrO_2 + CaCO_3 \quad (1)$$

$$Ca_2SiO_4 + 2CO_2 \leftrightarrow 2CaCO_3 + SiO_2 \quad (2)$$

$$M^{(n-1)+}\text{-}OH + CO_2 \leftrightarrow M^{(n-1)+}\text{-}HCO_3 \quad (3)$$

$$M^{n+} \leftarrow H_2O + CO_2 \leftrightarrow M^{n+} \leftarrow H_2CO_3 \quad (4)$$

where, M^{n+} stands for the metal ion in the mixed metal oxides. Thus, the several reactions are occurring simultaneously and reversible could help to capture and release the CO_2 during the reactions. The hydroxyl groups and water molecules attached to the metal ions depend on the calcination, pre-treatment and activation temperatures before the use of an adsorbent to applications [2]. The conversion of CO_2 by methane to syn-gas could be given as follows:

$$CO_2 + CH_4 \leftrightarrow 2CO + 2H_2 \quad \Delta H=62.2 \text{ kcal.mol}^{-1} \quad (5)$$

3.1. Characterization of the Samples of Mixed Metal Oxides

3.1.1. The characterization of samples of the mixed metal oxides by XRD, surface area and acidity/basicity

The samples of mixed metal oxides had been characterized for the surface area, basicity/ acidity, SEM images and XRD patterns. The observed XRD patterns of the samples of calcium zirconium silicate which were prepared by different methods such as template, precipitation, solid-solid fusion and sol gel methods were used to characterize the materials (Figure 2a). The presented XRD patterns (Figure 2b) of the samples CZSF611, CZSF411, CZSF311 and CZSF111 of calcium zirconium silicate were prepared by the solid-solid fusion method with the different mol ratios (Ca:Zr:Si, 6:1:1, 4:1:1, 3:1:1 and 1:1:1) were used to assess the materials. The phases of the CaO, ZrO_2, SiO_2, calcium zirconate, calcium silicate, zirconium silicate and calcium zirconium silicate were observed (Figures 2a-2b). However, the crystalline phases of the $Ca_3Si_2O_7$, $CaZrO_3$ and Ca_2SiO_4 were pre-dominantly seen in the samples CZSF611, CZSF411 and CZSF311 when the Ca:Zr:Si, 6:1:1, 4:1:1 and 3:1:1 mol ratios were used while preparing the samples of calcium zirconium silicate. However, calcium rich phases in the samples of calcium zirconate silicate were not observed when the sample CZSF111 (Ca:Zr:Si, 1:1:1 mol ratios) was cha-

racterized. Figure 2c shows the XRD patterns of the samples of sodium aluminium silicate and calcium lanthanum oxide prepared by solid-solid fusion method with different mol ratio of Na:Al:Si (SAS611) and Ca:La (CL61).

The surface areas and basicity of the different samples of calcium zirconium silicate were used to analyse the material (Table 1). The metal content, method of preparation, calcination temperature, crystalline phase and pores formation etc. are the different factors contributed to the surface area. The samples CZSF111, CZSF311, CZSF411 and CZSF611 of calcium zirconium silicate with mol ratios Ca:Zr:Si, 1:1:1, 3:1:1, 4:1:1, 6:1:1 had surface area 49.1, 57.0, 104.7 and 138.76 $m^2.g^{-1}$, respectively. The results indicate that the samples of calcium zirconium silicate are porous materials with the depending on the surface area. The surface area of the samples of calcium zirconium silicate was varied from 21.32 to 138.76 $m^2\ g^{-1}$. The surface area was observed increased with the increased in the mol ratio of calcium from 1 to 6. The surface area of the samples also depends on the method of preparation of the samples. The basicity of the samples of calcium zirconium silicate was observed in between the 0.7 and 15.17 $mmol.g^{-1}$ depending on the method of the preparation and the mol ratio of calcium.

3.1.2. SEM images of some mixed metal oxides

The SEM images of some mixed oxides were taken to observe the particle pattern (Figure 3). The SEM images were shown of the samples CZSF111, CZSF311, CZSF411, CZSF611, CZSG611, CZST611 and CZSP611 of calcium zirconium silicate with mol ratios Ca:Zr:Si, 1:1:1, 3:1:1, 4:1:1, 6:1:1, the samples of CCTM611, CCTM411, CCTM211 and CCTM111 (by salt molten method), and CCTF611 (solid fusion) of calcium copper titanate and the samples CILF611 (solid fusion) of calcium iron lanthanide. The SEM images of calcium lanthanide oxide (Ca:La, 6:1) by solid fusion method and sodium aluminium silicate (Na:Al:Si, 6:1:1) by solid fusion method were taken (Figure 3). The images of these different samples show the grown uniform particle size of crystal particles. The changes in the morphology of the crystals were observed. The comparing the SEM images of the samples of mixed metal oxides from the Figure 3, it showed that the dominant growth of spherical-like particles was observed. This suggests that the growth of different crystal structure of the mixed metal oxides.

3.1.3. ^{29}Si NMR of some mixed metal oxide samples

Here, the ^{29}Si NMRs of the sample CZSF611 of calcium zirconium silicate (Figure 4a) and the sample CASF611 of calcium aluminium silicate (Figure 4b) were presented. The results of ^{29}Si NMR showed that the chemical shift had been moved toward -80 ppm. That indicated that the silicon is not in the tetrahedral bonded but it is with multi-bonded solid state [27-30]. The chemical shift shows that the chemical bonding is reoriented during the solid adsorbent formation.

3.2. CO_2 Capture

The CO_2 captured by the different phases could be related to the enthalpy of formation of different phases [2]. The more enthalpy is required for the formation of crystalline phase, then, for the CO_2 capture also more enthalpy is required for the formation of carbonate. These phases simultaneously more or less could be contributing to CO_2 capture. There were two peaks observed [2]. The first peak represented the physic-sorption of weakly bond CO_2. The second peak represented the chemisorptions of strongly bound CO_2. The observed results were given for the physic-sorption, chemisorptions and combined.

3.2.1. Calcium zirconium silicate

The results of the captured CO_2 by the samples CZSF111, CZSF311, CZSF411, CZSF611, CZST611, CZSG611 and CZSP661 of calcium zirconium silicates with mol ratios Ca:Zr:Si, 1:1:1, 3:1:1, 4:1:1, 6:1:1 at 700 ^oC were given to assess the CO_2 capturing capacity (Figure 5). The captured CO_2 was observed in between 7.36 to 25.35 wt.%. The basicity of these samples was observed in the range 0.7 to 15.17 $mmol.g^{-1}$ (Table 1). The CO_2 captured by these samples were observed in the increased mol ratio of calcium.

3.2.2. Calcium copper titanate

The samples CCTF111, CCTF211, CCTF 411 and CCTF611 of calcium copper titanate with mol ratios Ca:Cu:Ti, 1:1:1, 2:1:1, , 4:1:1, and 6:1:1 were tested for the CO_2 capture at 700 ^oC (Table 2). The CO_2 captured by the samples of calcium copper titanate was 9.82 to 19.66 wt.%. Moreover, the basicity was observed from 1.62 to 10.37 $mmol.g^{-1}$.

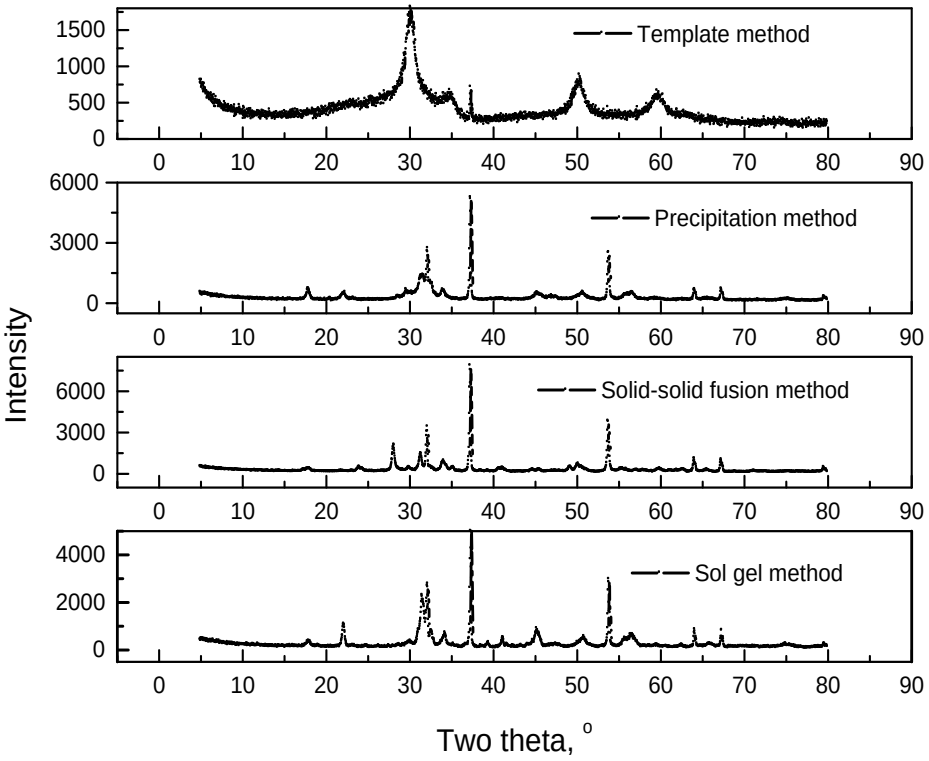

Figure 2. (a) The XRD pattern of the samples of calcium zirconium silicate prepared by different methods such as solid-solid fusion, precipitation, sol gel and template methods

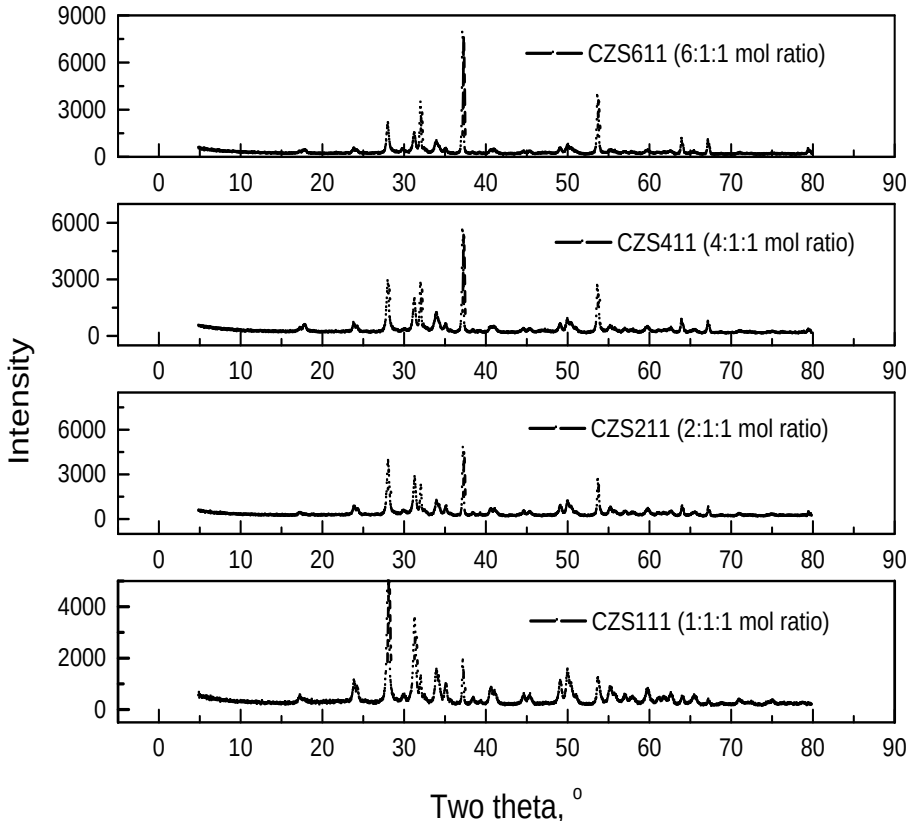

Figure 2. (b) The XRD pattern of the samples of calcium zirconium silicate prepared by solid-solid fusion method with different mol ratio of Ca:Zr:Si

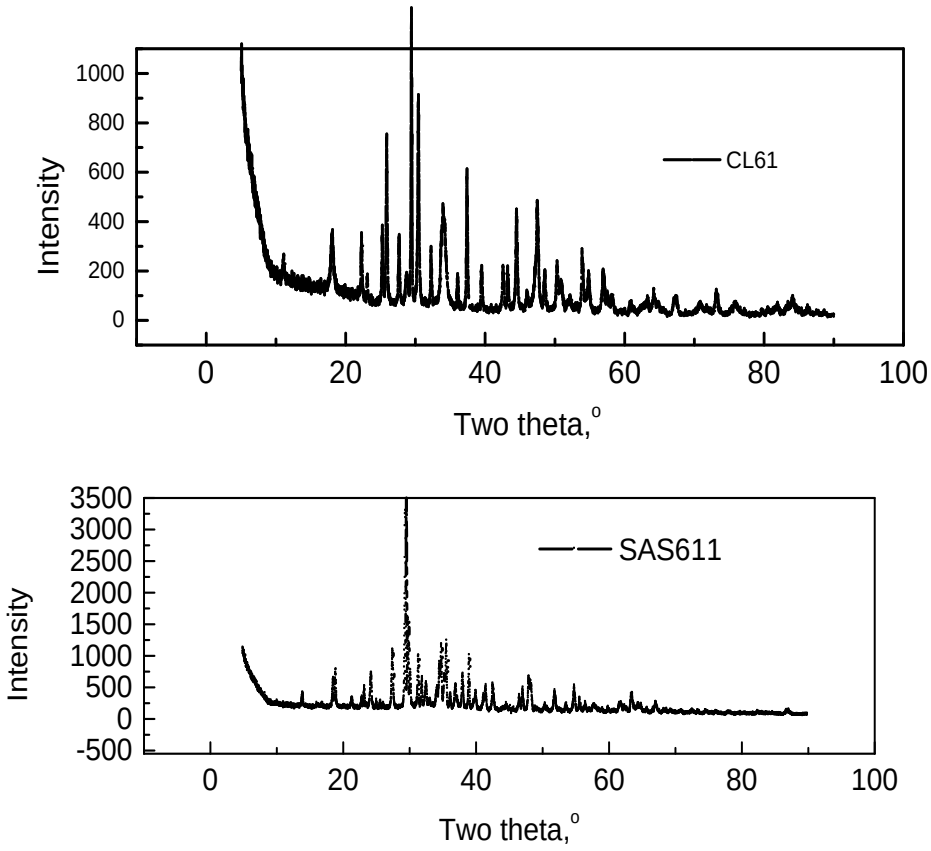

Figure 2. (c) The XRD pattern of the samples of sodium aluminum silicate and calcium lanthanum oxide prepared by solid-solid fusion method with different mol ratio of Na:Al:Si (SAS611) and Ca: La (CL61).

Table 1. The basicity and surface area of the samples of calcium zirconium silicate

Sr. No	Adsorbent	Alkalinity, mmol/g	Surface area, $m^2.g^{-1}$
1	CZSF 111 (Solid fusion)	4.31	49.1
2	CZSF 211 (Solid fusion)	8.79	57.0
3	CZSF 411 (Solid fusion)	13.15	104.7
4	CZSF 611 (Solid fusion)	15.17	138.76
5	CZSG 111 (Sol-gel)	9.18	16.21
6	CZSG 211 (Sol-gel)	10.20	18.9
7	CZSG 411 (Sol-gel)	12.60	20.85
8	CZSG 611 (Sol-gel)	14.54	24.21
9	CZSP611 (Precipitation)	14.03	22.24
10	CZST611 (Template)	0.70	21.32

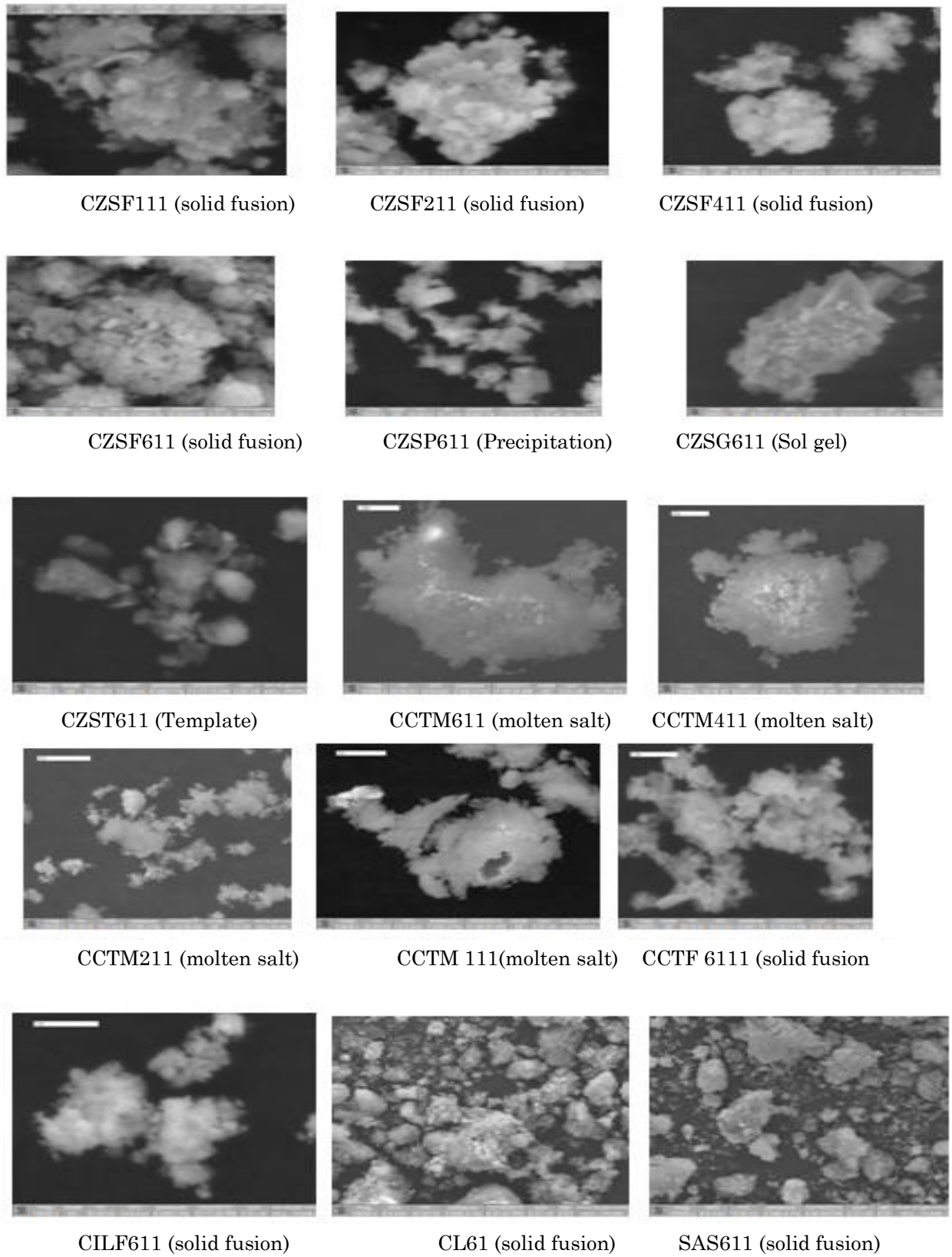

Figure 3. The SEM images of the samples of calcium zirconium silicate (Ca:Zr:Si, different mol ratios) prepared by different methods and also the SEM images of the samples of calcium copper titanate (Ca:Cu:Ti, different mol ratio) prepared by molten salt and solid-solid fusion method, calcium lanthanide oxide (Ca:La, 6:1) by solid fusion method and sodium aluminium silicate (Na:Al:Si, 6:1:1) by solid fusion method.

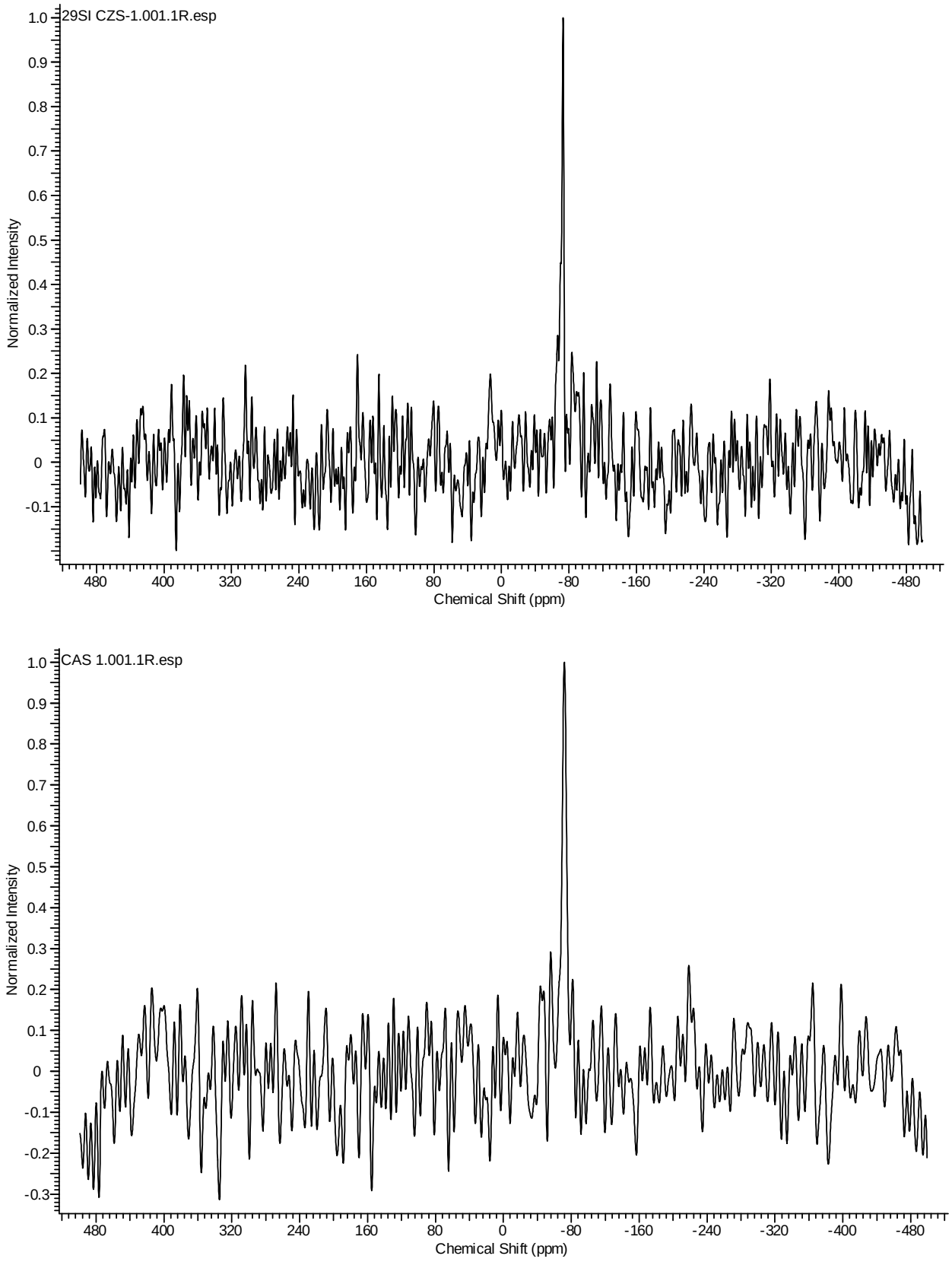

Figure 4. (a) ^{29}Si NMR of the sample CZSF611 of calcium zirconium silicate prepared by solid-solid fusion method; (b) ^{29}Si NMR of the sample CASF611 of calcium aluminium silicate prepared by solid-solid fusion from calcium oxide, aluminium oxide and silica oxide

Table 2. The captured CO_2 at 300 or 700 ^oC and the alkalinity of adsorbents

Sr. No	Adsorbent	Alkalinity (mmol/g)	Captured CO_2 at 300 or 700 ^0C, wt.%		
			Physisorption	Chemisorptions	Combined
	Calcium zirconium silicate			at 700 ^oC	
1	CZSF611 (solid fusion)	15.17	0.93	21.04	21.97
2	CZSF411 (solid fusion)	13.15	0.86	14.21	15.07
3	CZSF211(solid fusion)	8.79	0.86	13.22	14.08
4	CZSF111(solid fusion)	4.31	1.08	10.72	11.80
5	CZSG611(sol gel)	14.54	0.88	14.57	15.45
6	CZSG411(sol gel)	12.60	0.81	14.42	15.23
7	CZSG211(sol gel)	10.20	0.60	13.00	13.60
8	CZSG111(sol gel)	9.18	0.51	12.2	12.71
9	CZSP611 (precipitation)	14.03	1.04	24.32	25.35
10	CZST611(template)	0.70	-	-	7.36
	Calcium copper titanate				
11	CCTF611 (solid fusion)	10.37	1.08	18.58	19.66
12	CCTF411 (solid fusion)	8.77	0.77	15.11	15.88
13	CCTF211 (solid fusion)	6.27	0.97	14.48	15.45
14	CCTF111(solid fusion)	1.63	0.80	9.03	9.82
15	CCTMS611 (molten salt)	2.28	0.96	10.20	11.15
	Calcium iron lanthanide				
16	CILF611(solid fusion)	11.02	0.64	26.29	26.93
17	CILF411(solid fusion)	10.63	0.61	20.20	20.81
18	CILF211(solid fusion)	6.89	0.92	11.25	12.17
19	CILF111(solid fusion)	2.27	0.60	10.29	10.89
	Calcium aluminum silicate				
20	CASF611(solid fusion)	10.23	0.82	16.85	17.67
21	CASF411(solid fusion)	6.122	0.95	16.37	17.32
22	CASF211(solid fusion)	5.00	1.11	12.85	13.96
23	CASFH111(solid fusion)	3.09	0.86	8.32	9.18
24	CASFNH611 (solid fusion)	9.40	0.84	13.2	14.04
	Magnesium nickel silicate				
25	MNSF611 (solid fusion)	1.51	5.72	-	5.72
26	MNSF411 (solid fusion)	1.35	5.69	-	5.69
27	MNSF211 (solid fusion)	1.09	5.66	-	5.66
28	MNSF111 (solid fusion)	0.71	5.44	-	5.44
	Calcium lanthanum oxide				
29	CLF61 (solid fusion)	17.25	0.08	44.37	44.45
30	CLF41(solid fusion)	17.18	0.85	43.58	44.43
31	CLF21(solid fusion)	14.39	0.60	34.60	35.20
32	CLF11(solid fusion)	9.74	0.72	27.54	28.26
	Sodium aluminum silicate	At 300 ^oC			
33	SAS611(solid fusion)	5.83	0.71	14.06	14.78
34	SAS411(solid fusion)	3.39	0.32	6.19	6.52
35	SAS211(solid fusion)	2.28	0.15	4.59	4.74
36	SAS111(solid fusion)	0.27	0.083	3.40	3.48

3.2.3. Calcium iron lanthanide

The captured CO_2 by the samples CILF611, CILF411, CILF211 and CILF111 of calcium iron lanthanum with Ca:Fe:La, 6:1:1, 4:1:1, 2:1:1 and 1:1:1 mol ratios were given at 700 °C (Table 2). The CO_2 captured by the samples of calcium iron lanthanide was 10.89 to 26.93 wt.%. Moreover, the basicity was observed from 2.27 to 11.02 mmol.g^{-1}.

3.2.4. Calcium aluminum silicate

The samples CASF611, CASF411, CASF211 and CASF111 of calcium aluminium silicate with Ca:Al:Si, 6:1:1, 4:1:1, 2:1:1 and 1:1:1 mol ratios were used to capture CO_2 at 700 °C (Table 2). The CO_2 captured by the samples of calcium aluminium silicate was 9.18 to 17.67 wt.%. Moreover, the basicity was observed from 3.09 to 10.23 mmol.g^{-1}.

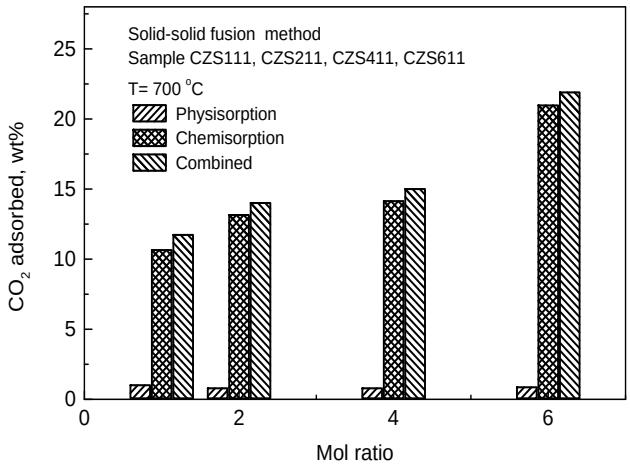

Figure 5. The profile of captured CO_2 by the sample of calcium zirconium silicate prepared by solid-solid fusion method with variable mol ratio

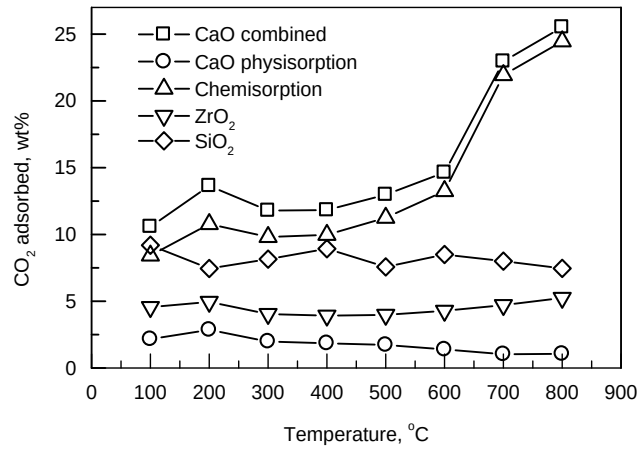

Figure 6. The temperature profile of captured CO_2 by the CaO, ZrO_2 and SiO_2

3.2.5. Magnesium nickel silicate

The samples MNSF611, MNSF411, MNSF211, and MNSF111 of magnesium nickel silicate with Mg:Ni:Si, 6:1:1, 4:1:1, 2:1:1 and 1:1:1 mol ratios were explored for the capture of CO_2 at 700 °C (Table 2). The CO_2 captured by the samples of magnesium nickel silicate was 5.44 to 5.77 wt.%. Moreover, the basicity was observed from 0.71 to 1.51 mmol.g^{-1}. The results of the captured CO_2 showed that the captured CO_2 by the samples of adsorbent depend the basicity of adsorbent (Table 2).

3.2.6. Calcium lanthanum oxide

The results of the captured CO_2 by the samples CLF61, CLF41, CLF21 and CLF11 of the calcium lanthanum oxide were presented at 700 °C (Table 2). The captured CO_2 by these samples was observed in the range 0.08 to 44.45 wt.%. The basicity of these samples was observed in the range 9.74 to 17.25 mmol.g^{-1}.

3.2.7. Sodium aluminium silicate

The results of the captured CO_2 by the samples SASF61, SASF41, SASF21 and SASF11 of the sodium aluminium silicate were presented at 300 °C (Table 2). The captured CO_2 by these samples was observed in the range 0.083 to 14.78 wt %. The basicity of the samples of sodium aluminium silicate was observed in between 0.27 to 5.83 mmol.g^{1}. In the overall results of captured CO_2 by the samples of mixed metal oxides showed the captured CO_2 was enhanced by increased basicity of mixed metal oxide.

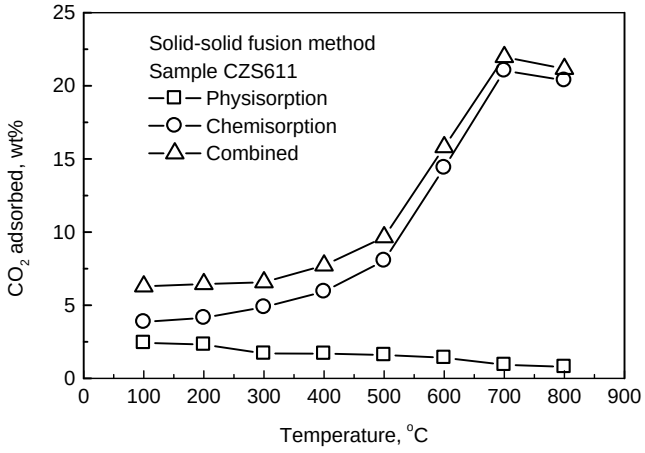

Figure 7. The temperature profile of captured CO_2 by the sample CZSF611 of calcium zirconium silicate prepared by solid-solid fusion method

3.3. Temperature Profile for CO_2 Capture

3.3.1. Calcium oxide, zirconium oxide and silicon dioxide

The temperature profile of captured CO_2 (Figure 6) by the samples of SiO_2, ZrO_2 and CaO are given. The CaO showed the captured CO_2 by physic-sorption in the range from 1.08 to 2.88 wt.%, chemisorptions of 8.42 to 24.48 wt.% and combined of 10.58 to 25.52 wt.%. However, the ZrO_2 captured CO_2 in the range from 3.93 to 5.25 wt.%. Moreover, the captured CO_2 by the sample of SiO_2 was in the range from 7.45 to 9.19 %.

3.3.2. Calcium zirconium silicate

The temperature profiles (Figures 7-10) of captured CO_2 by the sample CZSF611 of calcium zirconium silicate with mol ratio (Ca:Zr:Si, 6:1:1) prepared by different methods solid-solid fusion, precipitation, sol gel and template methods were presented for the temperature range from 100 to 850 ^oC. The data of the captured CO_2 was presented in terms of physic-sorption, chemisorptions and combined sorption. The observed CO_2 captured by the different phases of calcium zirconium silicate could depend on the enthalpy of formation of different phases. For those phases, the carbonate formation could also depend on the enthalpy of carbonate formation. The CO_2 sorption by the sample of calcium zirconium silicate was observed in two major temperature zones. The first CO_2 sorption zone was from 100 to 400 ^OC, where the physic-sorption was higher. The second CO_2 sorption zone was found from the range of 500 to 700 ^oC, where the chemisorptions were higher. The physic-sorption was in the range from 0.57 to 1.78 wt.%. However, the chemisorptions were in the range from 7.22 to 24.32 wt.%. The captured CO_2 by the sample of calcium zirconium silicate showed the formation of calcium carbonate and released the silica and zirconia. The reversible reactions were also observed at higher temperature. Therefore, calcium zirconium silicate mixed metal oxides are the regenerable adsorbent for CO_2.

3.3.3. Calcium copper titanate

The temperature profile of captured CO_2 (Figure 11) by the sample CCTF611 of calcium copper titanate with mol ratio (Ca:Cu:Ti, 6:1:1) was presented for the temperature range from 100 to 850 ^oC. The data of the captured CO_2 was presented in terms of physic-sorption, chemisorptions and combined sorption. The CO_2 sorption by the sample of calcium copper titanate was observed in two major temperature zones. The first CO_2 sorption zone was from 100 to 400 ^OC, where the physic-sorption was higher. The second CO_2 sorption zone was found from the 500 to 700 ^oC ranges, where the chemisorptions were higher.

The physic-sorption was in the range from 1.08 to 2.44 wt.%. However, the chemisorptions were in the range from 5.69 to 18.58 wt %. In the first temperature CO_2 sorption zone from 100 to 400 ^OC, the CO_2 sorption by the sample of calcium copper titanate was from 8.04 to 8.13 wt.%. However, in the second temperature zone from 500 to 700 ^oC, the CO_2 sorption was ranged from 8.68 to 19.66 wt.%. In the temperature range from 500 to 700 ^oC, the CO_2 sorption by the sample of calcium copper titanate showed the formation of calcium, copper and titanate carbonate. The reversible reac-

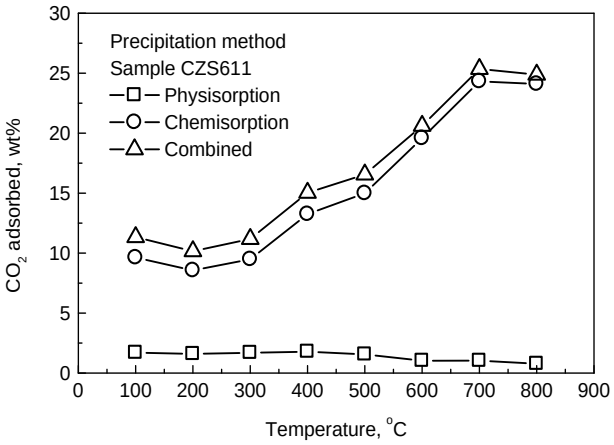

Figure 8. The temperature profile of captured CO_2 by the sample CZSP611 of calcium zirconium silicate prepared by precipitation method

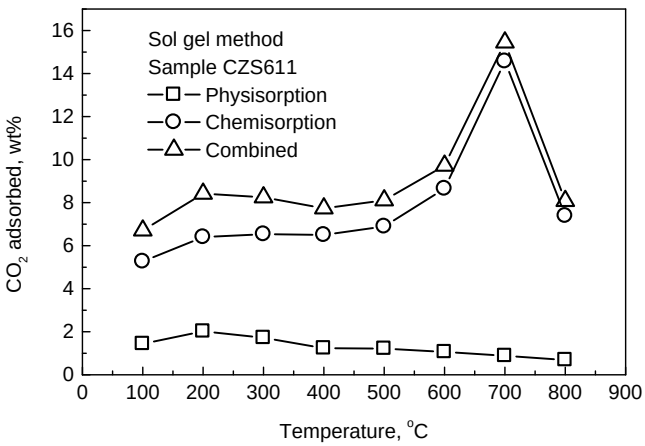

Figure 9. The temperature profile of captured CO_2 by the sample CZSG611 of calcium zirconium silicate prepared by sol-gel fusion method

tions were also observed in this temperature zone. Therefore, calcium copper titanate mixed metal oxides are the regenerable adsorbent for CO_2.

3.3.4. Calcium iron lanthanide

The temperature profile of captured CO_2 by the sample CILF611 of calcium iron lanthanum with mol ratio (Ca:Fe:La, 6:1:1) was presented for the temperature range from 100 to 850 °C (Figure 12). The data of the captured CO_2 was presented in terms of physic-sorption, chemisorptions and combined sorption. The CO_2 sorption by the sample of calcium iron lanthanum was observed in two major temperature zones. The first temperature CO_2 sorption zone was ranged from 100 to 400 °C, where the physic-sorption was higher. The second temperature CO_2 sorption zone was found from to 700 °C, where the chemisorptions were higher. The physic-sorption was in the range from 0.64 to 1.41 wt.%. However, the chemisorptions were in the range from 7.25 to 26.93 wt.%. In the first temperature CO_2 sorption zone from 100 to 400 °C, the CO_2 sorption by the sample of calcium iron lanthanum was from 5.92 to 6.82 wt.%. However, in the second temperature zone from 500 to 700 °C, the CO_2 sorption was ranged from 7.2 to 26.29 wt.%. In the temperature range from 500 to 700 °C, the CO_2 sorption by the sample of calcium iron lanthanum showed the formation of calcium, iron and lanthanum carbonates. The reversible reactions were also observed in this temperature zone. Therefore, calcium iron lanthanum mixed metal oxides are the regenerable adsorbent for CO_2.

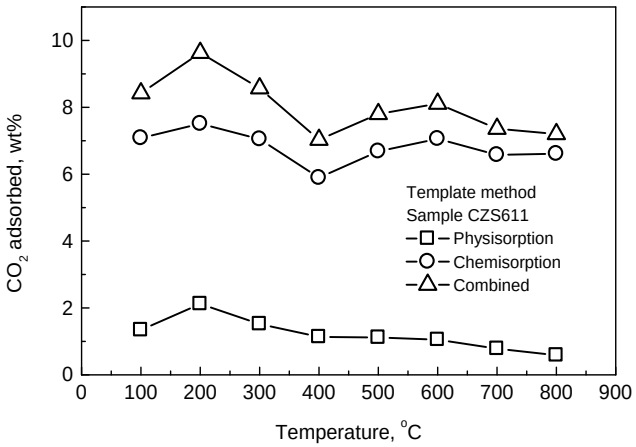

Figure 10. The temperature profile of captured CO_2 by the sample CZST611 of calcium zirconium silicate prepared by template method

3.3.5. Calcium aluminium silicate

The temperature profiles (Figures 13a-13b) of captured CO_2 by the sample CASF611 of calcium aluminium silicate with mol ratio (Ca:Al:Si, 6:1:1) were given. The sample of calcium aluminium silicate was prepared (Figure 13a) by using CaO, Al_2O_3 and SiO_2. The sample (Figure 13b) of calcium aluminium silicate was prepared by using $Ca(NO_3)_2$, aluminium hydroxide and fumed silica. The temperature profiles of captured CO_2 by the samples were presented for the temperature range from 100 to 850 °C. The data of the captured CO_2 was presented in terms of physic-sorption, chemisorptions and combined sorption. The CO_2 sorption by the sample of calcium aluminium silicate was observed in two major temperature zones. The first CO_2 sorption zone was ranged from 100 to 400 °C, where the physic-sorption was higher. The second CO_2 sorption zone was

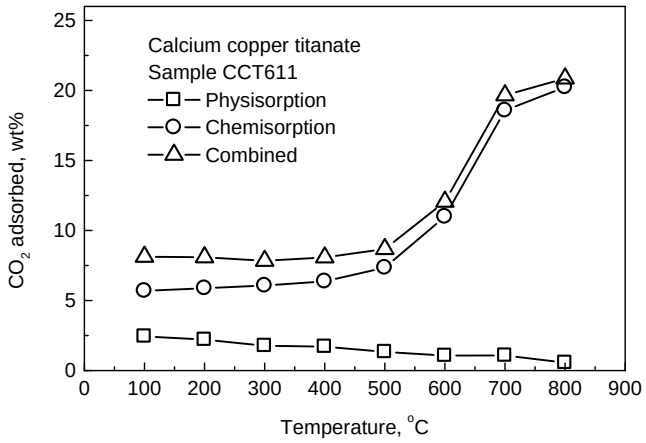

Figure 11. The temperature profile of captured CO_2 by the sample CCTF611 of calcium copper titanate

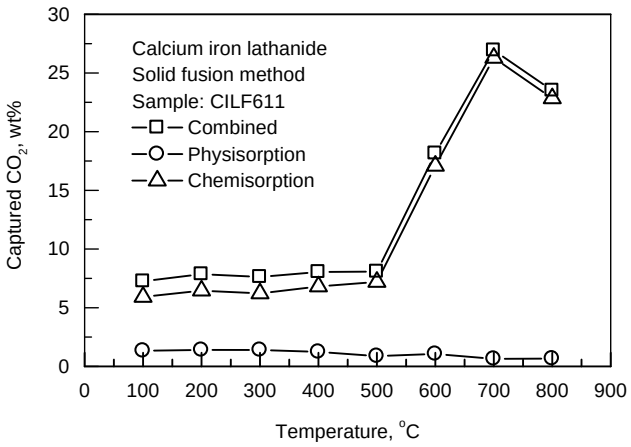

Figure 12. The temperature profile of captured CO_2 by the sample CILF611 of calcium iron lanthanide

found from the range of 500-700 °C, where the chemisorptions were higher. The physic-sorption was in the range from 0.84 to 1.69 wt.%. However, the chemisorptions were in the range from 5.52 to 13.27 wt.%. In the first temperature CO_2 sorption zone of 100-400 °C, the CO_2 sorption by the sample of calcium aluminium silicate was ranged from 6.68 to 7.89 wt.%. However, in the second temperature zone of 500-700 °C, the CO_2 sorption was ranged from 8.55 to 14.27 wt.%. In the temperature range of 500-700 °C, the CO_2 sorption by the sample of calcium aluminium silicate showed the formation of calcium carbonate and released the silica and alumina. The reversible reactions were also observed in this temperature zone. Therefore, calcium aluminium silicate mixed metal oxides are the regenerable adsorbent for CO_2.

3.3.6. Magnesium nickel silicate

The temperature profile (Figure 14a) of captured CO_2 by the magnesium oxide was taken. The physic-sorption by MgO was in the range from 5.75 to 7.92 wt.%. However, the chemisorptions were in the range from 0.5 to .97 wt.%.

The temperature profile of captured CO_2 by the sample MNSF611 of magnesium nickel silicate with mol ratio (Mg:Ni:Si, 6:1:1) was (Figure 14b) presented for the temperature range from 100 to 850 °C. The CO_2 sorption by the sample of magnesium nickel silicate was observed in two major temperature zones. The first CO_2 sorption was ranged from 100 to 400 °C, where the physic-sorption was higher. The second CO_2 sorption zone was observed from

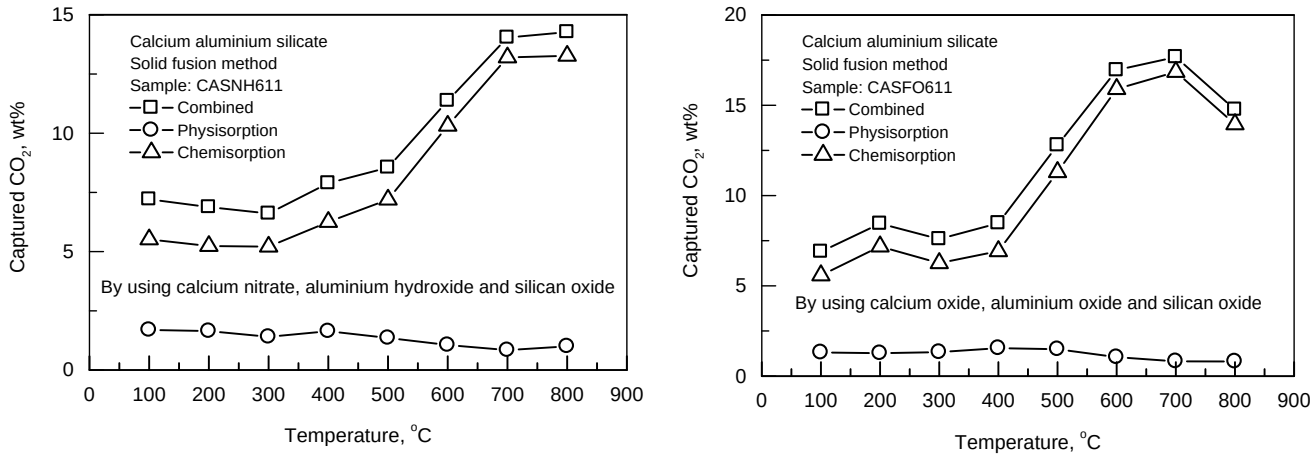

Figure 13. (a) The temperature profile of captured CO_2 by the sample CASFNH611 of calcium aluminium silicate by using calcium nitrate, aluminium nitrate and silicon oxide; (b) The temperature profile of captured CO_2 by the sample CASFO611 of calcium aluminium silicate by using calcium oxide, aluminium oxide and silicon oxide

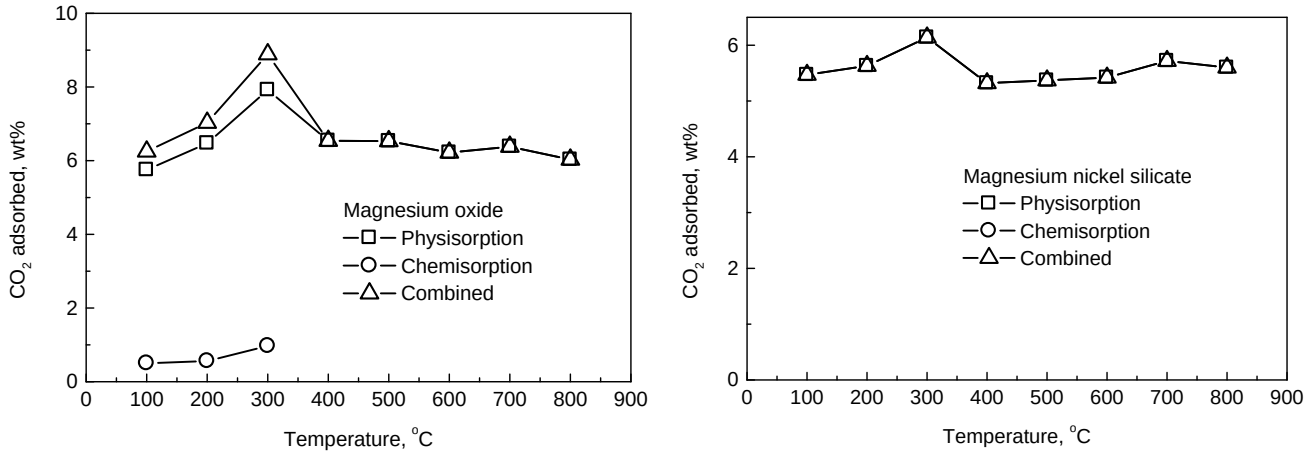

Figure 14. (a) The temperature profile of captured CO_2 by the magnesium oxide; (b) the temperature profile of captured CO_2 by the sample MNSF611 of magnesium nickel silicate

the 500 to 700 °C, where the physic-sorption was lower. The physic-sorption was in the range from 5.47 to 6.14 wt.%.

3.3.7. Calcium lanthanum oxide

The temperature profile (Figure 15a) of captured CO_2 by the sample CL61 (Ca:La, 6:1) of calcium lanthanum oxide has been taken. The results of captured CO_2 by the sample CL61 of calcium lanthanum oxide had been observed with the form of physic-sorption and chemisorptions. However, the chemisorptions had been observed in the temperature range 100 to 800 °C. The combined captured CO_2 was varied in between 4.21 and 44.45 wt.%.

3.3.8. Sodium aluminium silicate

The temperature profile of captured CO_2 by the sample SAS611 (Na:Si:Al, 6:1:1) of sodium aluminium silicate was (Figure 15b) shown for the temperature range of 100 to 800 °C. The captured CO_2 by the sample SAS611 was observed in the form of physic-sorption and chemisorptions. The chemisorptions from 12.93 to 14.06 were found to be in the temperature range 100 to 300 °C. However, physic-sorption was in the range from 0.29 to 4.6 wt.%. Moreover, the chemisorptions were declined in the temperature range of 400 to 600 °C. Above temperature 600 °C, the captured CO_2 was increased.

The samples of mixed metal oxide were tested for the regeneration test by using the same sample for several times. The results showed that the mixed metal oxide sample could be used for regeneration. Among the mixed metal oxides, the captured CO_2 by the samples of calcium lanthanum oxide was in the range of 28.26 to 44.45 wt.%. The obtained results had shown that the calcium lanthanum mixed metal oxides were found to be efficient material to capture CO_2 at higher temperatures. However, the efficiency of mixed metal oxides to capture CO_2 could be arranged in the increased order as sodium aluminium silicate < magnesium nickel silicate < calcium aluminium silicate< calcium copper titanate < calcium zirconium silicate < calcium iron lanthanide < calcium lanthanum oxides.

3.4. The Conversion of CO_2 by Methane to Syn-gas over Mixed Metal Oxides

The mixed metal oxide adsorbents were tested for the conversion of methane by CO_2 to syn-gas. However, the efficient mixed metal oxide adsorbents have been reported here. The catalytic conversion of CO_2 by methane to syn-gas is an endothermic reaction (Equation 5). The both CO_2 and CH_4 are thermally stable molecules. The activation energy required for the both molecules is high. Therefore, the thermal energy in the form of heat should be supplied to these CO_2 and methane molecules for the activation in the presence of catalyst. Since, the catalytic reaction of CO_2 with methane is an endothermic; the reaction should be carried out at high temperature by taking the advantage of coal gasification or coal combustion system in the thermal power stations such as post-combustion or pre-combustion temperatures. Moreover, in the thermal power plant, the flue gases contain the methane and CO_2 at either post or pre-combustion conditions. In addition to this, the mixed metal oxide adsorbents are

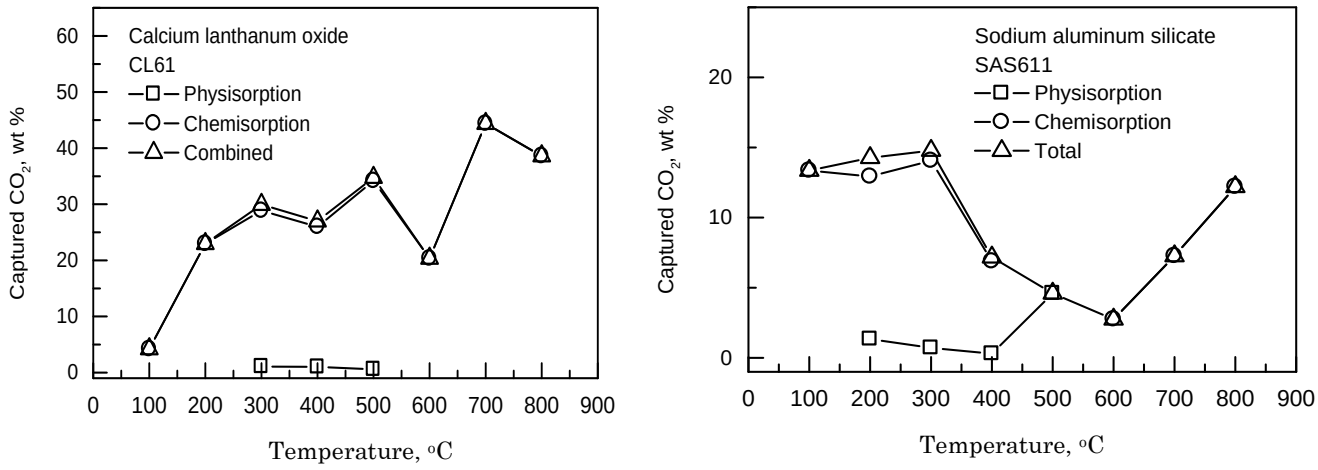

Figure 15. (a) The temperature profile of captured CO_2 by the sample of CL61 of calcium lanthanum oxide; (b) The temperature profile of captured CO_2 by the sample of SAS611 of sodium aluminium silicate

Table 3. The conversion of CO_2 by methane over mixed metal oxide adsorbent and (5 wt.%) Pd/Al_2O_3 at 700 ^oC by using the gas hourly space velocity of CO_2 = 6000 $ml.h^{-1}.g^{-1}$, CH_4 = 6000 $ml.h^{-1}.g^{-1}$ and He = 24000 $ml.h^{-1}.g^{-1}$

Sr. No	Catalyst	CO_2 conversion, %	CH_4 conversion, %	CO selectivity, %
1	(5 wt.%) Pd/Al_2O_3	48.83	33.34	51.78
Calcium zirconium silicate				
2	CZSF611	1.41	0.97	1.5
3	CZSF411	2.11	1.45	2.26
4	CZSF211	0.69	0.47	0.73
5	CZSF111	0.64	0.44	0.68
6	CZSP611	1.32	0.91	1.42
Calcium copper titanium oxide				
7	CCTF611	0.58	0.39	0.64
8	CCTF 411	0.41	0.28	0.47
9	CCTF211	0.32	0.22	0.35
10	CCTF111	0.14	0.10	0.15
Calcium iron lanthanum oxide				
11	CILF611	22.1	19.33	23.69
12	CILF411	15.85	13.86	16.99
13	CILF211	0.51	0.35	0.54
14	CILF111	0.26	0.18	0.28
Calcium aluminum silicate				
15	CASF611	2.31	1.60	2.48
16	CASF411	0.66	0.45	0.70
17	CASF211	0.31	0.21	0.32
18	CASF111	0.25	0.17	0.27
Magnesium nickel silicate				
19	MNS611	2.76	1.96	2.96
20	MNS411	0.56	0.38	0.59
21	MNS211	0.35	0.24	0.37
Calcium lanthanum oxide				
22	CL611	1.98	1.36	2.12

thermally stable at post- and pre- combustion temperatures and capture the CO_2. Therefore, the mixed metal oxide adsorbent could be, simultaneously, used for the CO_2 capture and conversion of CO_2 by methane to syn-gas. The syn-gas is used in the Fischer-Tropsch reaction for the conversion into hydrocarbons. Thus, at the high temperature, the mixed metal oxide adsorbents could be used for the both purposes for the CO_2 capture and conversion to syn-gas. Moreover, one mol of CO_2 and methane produces the two moles of each of CO and H_2. The supported catalysts magnesium-nickel, cobalt, iron, platinum, ruthenium, rhodium, molybdenum and vanadium reported for the dry reforming (conversion of methane by CO_2) of methane were found to be efficient. In order to test the mixed metal oxide CO_2 adsorbents for the dry-reforming of methane, the several experiments were carried out. However, the results of the dry-reforming of methane observed were reported here. The mixed metal oxide adsorbents were explored for the conversion of CO_2 by methane at higher temperature. However, the samples of calcium iron lanthanum mixed metal oxide and (5 wt.%) Pd/Al_2O_3 catalysts were explained here which found to be efficient catalysts for the dry-reforming of methane by CO_2.

3.4.1. Calcium iron lanthanide

The CO_2 conversion by methane (Table 3) over the different samples CILF611, CILF411, CILF211 and CILF111 of calcium iron lanthanum with Ca:Fe:La, 6:1:1 and 4:1:1 mol ratios were observed at 700 ^oC. The result of CO_2 conversion by methane was observed in between 15.85 to 22.1 %, methane conversion of 13.86-19.33 % and CO selectivity of 16.99-23.69 %.

3.4.2. (5 wt.%) Pd/Al_2O_3

The palladium 5 wt.% supported over alumina was tested for the conversion of CO_2 by methane at 700 ^oC. The results of conversion of CO_2 and methane; and the CO selectivity were useful for the conversion CO_2 to value added products (Table 3). The CO_2 and methane conversions were 48.83 % and 33.34 %, respectively. However, the CO selectivity was 51.78 %.

4. Conclusion

The mixed metal oxides included the calcium zirconium silicate, calcium aluminium silicate, calcium copper titanate, calcium iron lanthanide were tested to CO_2 capture. The different samples of calcium zirconium silicate, calcium aluminium silicate, calcium copper titanate and calcium iron lanthanide were prepared by sol-gel, precipitation, molten salt, template and solid-solid fusion methods. The samples of calcium zirconium silicate were characterized by basicity and surface area measurement, XRD patterns and SEM images. The basicity and CO_2 sorption of the samples of the calcium zirconium silicate increases with the increased in calcium mol in the Ca:Zr:Si mol ratio of the samples of calcium zirconium silicate from 1 to 6. The conversion of CO_2 by methane over mixed metal oxides was checked at 700 ^oC. The results showed that the (5 wt.%) Pd/Al_2O_3 and calcium iron lanthanum oxide were found to be efficient catalysts for the conversion of CO_2 by methane to syn-gas.

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