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Research Article

The Uses of Copper and Zinc Aluminates to Capture and Convert Carbon Dioxide to Syn-gas at Higher Temperature

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Abstract

The uses of copper and zinc aluminates to capture and convert the CO_2 to syn-gas were studied at higher temperatures. The samples of copper and zinc aluminates were prepared by solid-solid fusion method by calcining in air at 900 °C for 3 h. Those samples were characterized by acidity/alkalinity, surface area, XRD pattern, IR, SEM images and screening to capture CO_2 at the different temperatures. The phases Cu_2O, CuO, ZnO, $CuAl_2O_4$ and $ZnAl_2O_4$ were found to be in the samples of zinc and copper aluminates. Acidity and surface area of the samples of copper and zinc aluminates were found to be in the ranges from 0.063 to 9.37 mmol g^{-1} and 3.04 to 11.8 m^2 g^{-1}, respectively. The captured CO_2 by the samples of copper and zinc aluminates was found to be 19.92 to 31.52 wt% for the temperature range 40 to 850 °C. The captured CO_2 at 550 °C by variable Zn/Al and Cu/Al mole ratio from 0.5 to 6 of the samples of copper and zinc aluminates was found to be 12.81 to 18.04 wt%. The reduction of carbon dioxide by zinc and copper aluminates was observed. The conversion of CO_2 by methane over variable mole ratio of Cu/Al and Zn/Al in copper and zinc aluminates, respectively, at 500 °C showed the production of syn-gas by using the gas hourly space velocities (GHSV) 12000, 12000 and 6000 $ml.h^{-1}.g^{-1}$ of helium, CO_2 and methane. The conversions of CO_2 by methane over the samples of zinc and copper aluminates were studied at different mole ratios of CO_2 to methane.

Keywords: Captured CO_2; conversion of CO_2; copper and zinc aluminates; solid-solid fusion method; effect of temperature; effect of mole ratio

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1. Introduction

Due to high thermal stability and low activity of CO_2, the conversion in a single step of CO_2 to single value added product is seemed to be tough task. However, there is a possibility to convert the CO_2 to value added product through intermediate products. Therefore, an attempt has been made to improve the capturing CO_2 capacity of an adsorbent and then to convert the captured CO_2 to syn-gas. Then, the syn-gas could be converted to hydrocarbons. In the present environment scenario, the large amount of emitting gases such as sulfur dioxide, nitrous oxide, carbon monoxide and methane are causing the air and water pollution in large excess.

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The main sources of carbon dioxide are the fossil fuel combustion, aircraft, vehicles, refineries and natural gas combustion centers. In the atmosphere, day by day the concentration level of carbon dioxide is increasing from 250 to 390 ppm since the post industrial area. The excess acidic gases concentration in the atmosphere also causes acid rain and global warming. Therefore, the capture, sequestration and utilization of which the one of the green house gases carbon dioxide are important issues to be addressed. The reactions of CO_2 with the adsorbent involve the adsorption of CO_2 on the surface, in the pores (by capillary action) and carbonate formation. Amines and ionic liquids slowly react with CO_2, Carbon, zeolites, amines and ionic liquids are not suitable adsorbents at high temperature (> 450 ^oC) due to declined in CO_2 reaction. The mixed metal oxides react with CO_2 at higher temperature. Thermal stability of metal oxides is higher at post-and pre-combustion temperatures. The alkali and alkaline earth metal oxides react with CO_2 and form carbonates. The mixed metal oxide reactions with CO_2 are reversible and non-polluting including the mixed metal oxides are thermally stable. Therefore, mixed metal oxides for the reaction with CO_2 could be used at high temperature 500 to 1000 ^0C. The reaction of CO_2 with magnesium aluminum hydrotalcite [1-4] was explored in the temperature range 150 to 500 ^0C. Promoter effect of potassium and lithium by adding in lithium zirconate showed an enhanced reaction of carbon dioxide with lithium zirconate [5-18].

The copper-containing phases - copper oxide (CuO), cuprous oxide (Cu_2O), copper aluminate (spinel) ($CuAl_2O_4$), and cuprous aluminate (delafossite) ($CuAlO_2$) - were prepared by thermal reactions. The relative leachabilities of copper from these phases by 0.1 M HCl were found to be in the order $CuAl_2O_4 < CuAlO_2 << Cu_2O <$ CuO. The sintering and formation mechanism of phases $CuAl_2O_4$ and $CuAlO_2$ were reported. The report indicated that $CuAl_2O_4$ could be effectively formed between 850 and 950 ^oC by the gamma-alumina precursor. At higher temperatures, $CuAlO_2$ was produced only in the gamma-alumina system. The hypothesis that the spinel formation mechanism of copper aluminates has two stages supported by the results of changing Cu/Al mole ratio in the system, and the rate-limiting step was identified as the diffusion process in the second stage [19]. The spinel type zinc aluminate nanoparticles were prepared by a modified sol-gel method using aluminum nitrate, zinc ethylene di-amine complex, diethylene glycol monoethyl ether and citric acid. ZnO and $ZnAl_2O_4$ nanocrystals were obtained by heat treatment at 350 ^oC in air for 2 h. The formation of $ZnAl_2O_4$ was confirmed by the characterization by TGA, XRD, SEM and FTIR [20]. The spinel crystalline material $MgAl_2O_4$, $CuAl_2O_4$ and $ZnAl_2O_4$ formation, polymorphous transformations of alumina and sintering at higher temperature were investigated [21]. Zinc aluminate particles with average particles size of 40 nm were reported by synthesizing by using a sol-gel combustion method [22]. The zinc aluminate spinel structure stabilization and leaching of metal ions were explored [23]. The zinc and copper aluminates have extensively been studied for the synthesis of methanol from CO_2 and hydrogen [24-26]. Although, copper and zinc aluminates are industrial important catalysts, the studies on the captured CO_2 by zinc and copper aluminates are lacking. Therefore, this paper reports the capture of CO_2 and conversion to syn-gas by the samples of copper and zinc aluminates at higher temperatures.

2. Experimentals

2.1. Reagents, chemicals and apparatus

The chemicals copper, zinc and aluminum nitrate, sulfate, hydroxide, acetate and carbonate (Sigma-Aldrich), were used for preparation of samples of the copper and zinc aluminates. 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 copper and zinc aluminates (Thermax Co. Ltd). A split furnace (Carbolite USA) was used to carry the reaction of carbon dioxide with the samples of the copper and zinc aluminates at different temperatures. The products were analyzed by GC (Nucon India Ltd) with thermal conductivity and flame ion ionization detectors. The hydrogen analysis was done by GC by using argon as carrier gas and also hydrogen analyzer.

2.2. The preparation of the samples of copper and zinc aluminates

The samples of the copper and zinc aluminates were prepared by solid-solid fusion method for the different Cu: Al and Zn: Al mole ratios. While preparing the samples of the copper and zinc aluminates with Cu/Al, Zn/Al (6/1) mole ratio, 0.072 mol of zinc nitrate or copper nitrate and 0.012 mol of aluminum nitrate were used. The solid mass was thoroughly mixed and then calcined at 900 ^oC for 3 h. Zinc and copper oxides were prepared by calcining zinc and copper nitrates at 900 °C for 3 h. The samples of the copper and zinc aluminates prepared by the solid-solid fusion method with the different mole ratios were indicated as using their first letter and precursor first letter (copper = C, Zinc = Z, Aluminium = A, nitrate = n, hydroxide = h, sulfate = s, acetate = a, oxide = o, etc) such as CAnh61, CAnh41, CAnh31, CAnh21, CAnh11, ZAnn61, ZAnn41, ZAnn31, ZAnn21 and ZAnn11 (Cu : Al, Zn: Al, 6:1, 4:1, 3:1, 2:1 and 1:1). The different samples of copper or zinc aluminates were prepared by using different precursors of zinc, copper and aluminum. The particles -22 to -30 mesh sizes was used to capture CO_2 were prepared from the calcined solid mass.

2.3. Hydrothermal treatment

The prepared copper and zinc mixed metal oxide adsorbents were, in order to enhance the strong attachment of hydroxyl and water molecules to metal ions, thermally treated by using adsorbent to water 10 wt% ratio in a initially under vacuum rota-evaporator at 85 °C and then under vacuum in a vacuum oven at 300 °C for 12 h [27-36]. Before use to capture CO_2, each sample was pre-treated in helium atmosphere at that temperature for 30 min.

2.4. The characterizations of the samples of copper and zinc aluminates

Samples of the copper and zinc aluminates were characterized for the alkalinity/acidity, XRD patterns (Philips Power XRD), FTIR (Perkin Elmer Spectrum I), the surface area (Model Autosorb–1, Make- Quantachrome Instruments Pvt. LTD, USA) and SEM images (QUANTA 200 3D).

2.5. Procedure to capture CO_2

A gaseous set up was used to capture carbon dioxide with the samples of copper and zinc aluminates. The set up was designed 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. 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 center by using a quartz tube of the dimensions of 10 to 20 mm ID and 100 mm length. The sample of copper and zinc aluminates 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 copper and zinc aluminates was measured by using a thermocouple and temperature indicator. The quartz reactor was connected through four three ways gas valve and a gas sampling valve to GC by using stainless steel tubing connections. 0.05 to 0.1 g of the sample of copper and zinc aluminates with the particle size -22 to -30 meshes was used to capture CO_2. First, the sample of copper and zinc aluminates was flushed with helium gas in order to remove the stresses of other gases. Then, the sample of copper and zinc aluminates 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 copper and zinc aluminates in absence of helium at a certain pressure, temperature and time. Then, the reacted carbon dioxide with the sample of copper and zinc aluminates was removed by using helium as a carrier gas, and increasing the temperature of the sample of the copper and zinc aluminates bed to 900 °C. The removed carbon dioxide was analyzed by GC using a Porapak-Q column and thermal conductivity detector (Figure 1). The captured carbon dioxide by the sample of copper and zinc alumi-

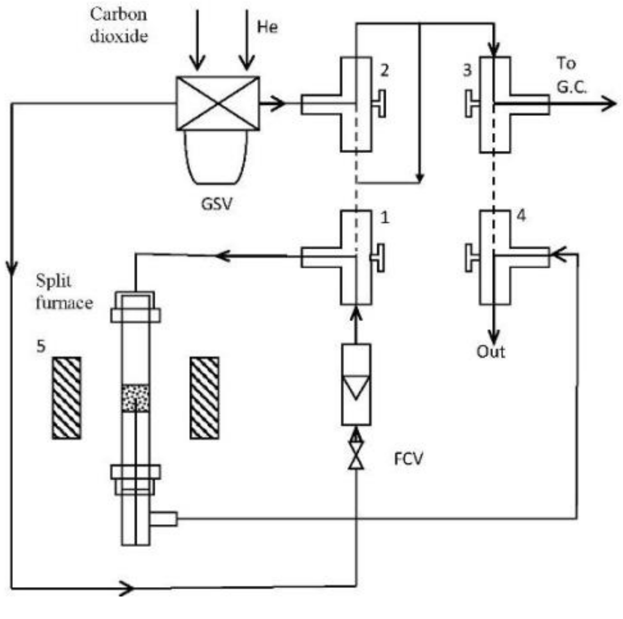


Figure 1. The systematic presentation of the on line set up for the capture of CO_2 and conversion to syn-gas, FCV = flow controlled valve, GC = gas chromatograph, 1,2,3,4 = three ways valves, 5 = split furnace and the quartz reactor and GSV = gas sampling valve

nates was expressed in wt% at STP.

2.6. Procedure to convert CO_2 to syn-gas

The conversion of carbon dioxide by methane was carried in the fixed bed quartz reactor. The system used was the same as described above but the system was set by changing the ways of gas through the three ways gas valves. The temperature of catalyst bed of copper and zinc aluminates in the fixed bed reactor with helium as carrier gas was set at a particular temperature with temperature controller. Then reaction gas mixture was introduced in the helium carrier gas in order to pass the reaction mixture through the catalyst bed. The outlet reacted gas mixture was analyzed by pulse method by using gas sampling valve connected on line system to GC with TCD and FID detectors. The results were reported here of conversion of CO_2 and methane and the selectivity to CO and H_2.

3. Results and Discussion

The possible reactions during the capture of CO_2 by copper and zinc aluminate could be given by the following equations. Copper and zinc carbonates decompose at high temperatures, giving off carbon dioxide and leaving copper and zinc oxides. The copper(II) oxide could be further reduced. The copper and zinc oxides also reduce the CO_2.

$$CuO + CO_2 \leftrightarrow CuCO_3 \quad (1)$$

$$2CuO \leftrightarrow Cu_2O + \tfrac{1}{2}\, O_2 \quad (2)$$

$$Cu_2O + CO_2 \leftrightarrow Cu_2CO_3 \quad (3)$$

$$CuAl_2O_4 + CO_2 \leftrightarrow CuCO_3 + Al_2O_3 \quad (4)$$

$$2CuAlO_2 + CO_2 \leftrightarrow Cu_2CO_3 + Al_2O_3 \quad (5)$$

$$ZnO + CO_2 \leftrightarrow ZnCO_3 \quad (6)$$

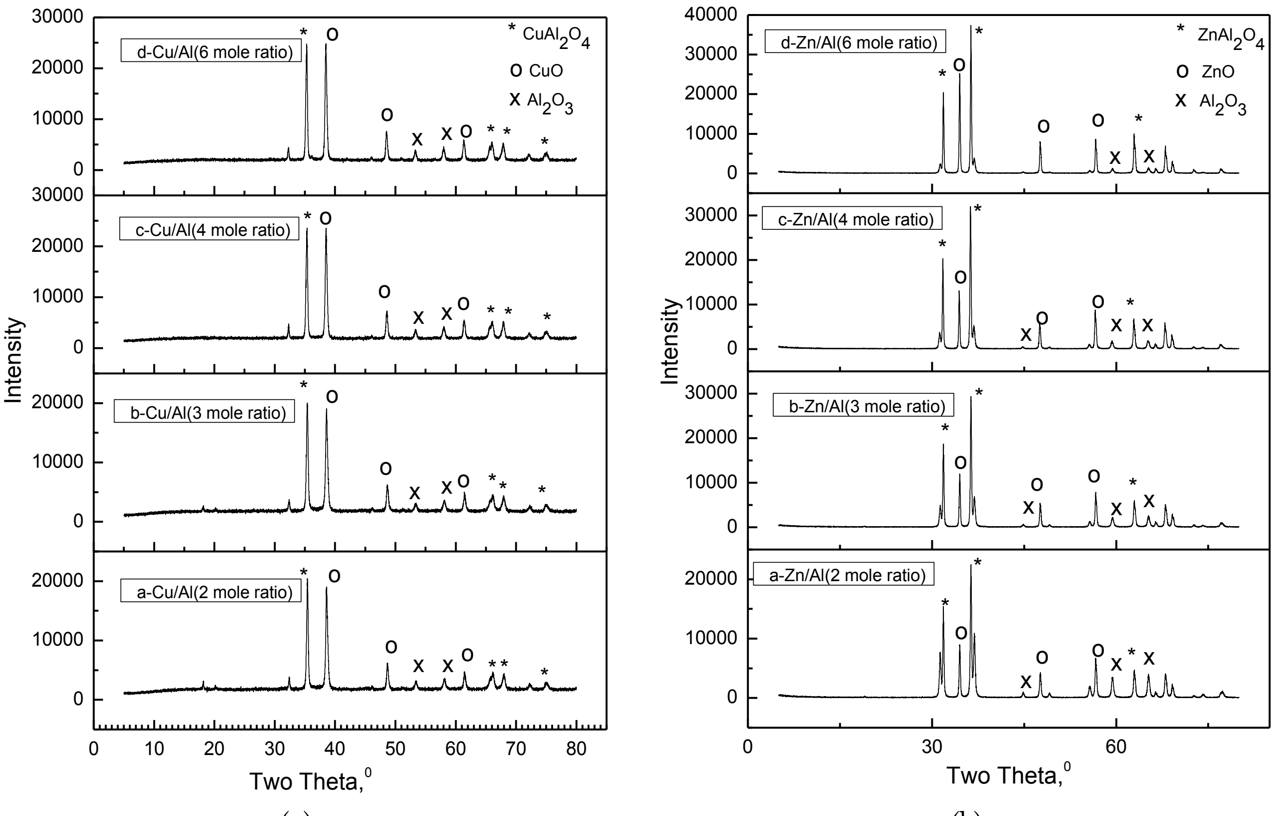
$$ZnAl_2O_4 + CO_2 \leftrightarrow ZnCO_3 + Al_2O_3 \quad (7)$$

$$2LiZnAlO_4 + 2CO_2 \leftrightarrow Li_2CO_3 + ZnCO_3 + Al_2O_3 \quad (8)$$

$$CuO + CO_2 \leftrightarrow CuO + C + O_2 \quad (9)$$

$$Cu_2O + CO_2 \leftrightarrow Cu_2O + C + O_2 \quad (10)$$

$$ZnO + CO_2 \leftrightarrow ZnO + C + O_2 \quad (11)$$



(a) (b)

Figure 2. The XRD patterns. (a) copper aluminates, CA61, CA41, CA31, and CA21 were prepared from copper nitrate and aluminum hydroxide with variable mole ratio by the solid-solid fusion method and calcined at 900 °C for 3 h in air; (b) The XRD pattern of the zinc aluminates, ZA61, ZA41, ZA31, and ZA21 were prepared from zinc nitrate, aluminum nitrate with variable mole ratio by the solid-solid fusion method and calcined at 900 °C for 3 h in air

The hydroxyl groups or water molecules present in the zinc and copper aluminates could help to capture CO_2:

$$M^{(n-1)+}\text{-}OH + CO_2 \leftrightarrow M^{(n-1)+}\text{-}HCO_3 \qquad (12)$$

$$M^{n+} \leftarrow H_2O + CO_2 \leftrightarrow M^{n+} \leftarrow H_2CO_3 \qquad (13)$$

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 application.

The conversion of CO_2 by methane to syngas could be given as:

$$CO_2 + CH_4 \leftrightarrow 2CO + 2H_2 - 62.2 \text{ kcal mol}^{-1} \qquad (14)$$

3.1. The characterization of the sample of copper and zinc aluminates

The samples of copper and zinc aluminates had been characterized for the surface area, alkalinity/acidity, FTIR, SEM images and XRD patterns. In the Figures 2 (a-b), the represented XRD patterns of the samples of the copper and zinc aluminates were prepared by the solid-solid fusion method with the different mole ratios CAnh61, CAnh41, CAnh31, CAnh21, ZAnn61, ZAnn41, ZAnn31 and ZAnn21 (Cu : Al, Zn: Al, 6:1, 4:1, 3:1 and 2:1). The phases of

Table 1. The surface area and acidity / alkalinity of the samples of copper and zinc aluminates

Sr. No.	Copper and zinc aluminates	Surface area, $m^2\ g^{-1}$	Acidity/ alkalinity, mmol g^{-1}
	Zinc aluminates with Zn/Al = 6 mole ratio		
1	Zinc nitrate and aluminum nitrate	5.45	0.58
2	Zinc nitrate and aluminum hydroxide	9.78	0.22
3	Zinc sulfate and aluminum nitrate	10.29	9.37
4	Zinc sulfate and aluminum hydroxide	11.80	9.33
	The effect of Zn/Al mole ratio on zinc aluminates prepared from zinc nitrate and aluminum nitrate		
5	2	3.04	0.063
6	3	3.89	0.114
7	4	4.01	0.398
8	6	5.45	0.580
	The effect of Cu/Al mole ratio on copper aluminates prepared from copper nitrate and aluminum hydroxide		
9	2	6.38	0.21 (alkalinity)
10	3	6.75	0.10 (alkalinity)
11	4	7.30	0.05 (alkalinity)
12	6	7.76	0.04 (alkalinity)

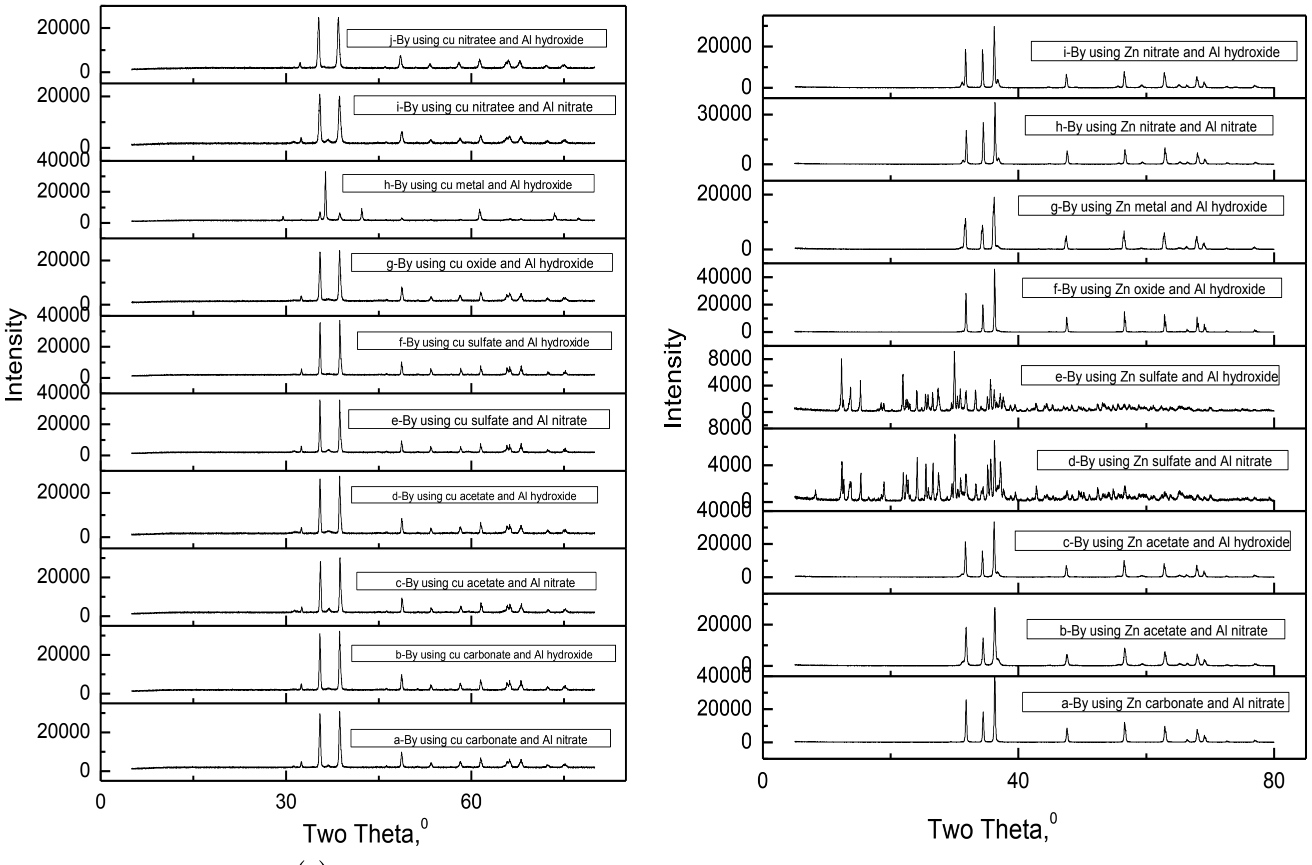
Table 2. The effect of different precursors on the captured CO_2 at 500 ^{0}C by the samples of copper and zinc aluminates with Cu/Al and Zn/Al = 6 mole ratio

Sr. No	The samples of copper and zinc aluminates with Cu/Al or Zn/Al = 6 mole ratio	Acidity/ Alkalinity mmol g^{-1}	Captured CO_2, wt %
	Zinc aluminates		
1	Zinc nitrate and aluminum nitrate	0.58	23.63
2	Zinc nitrate and aluminum hydroxide	0.22	23.32
3	Zinc sulfate and aluminum nitrate	9.37	23.38
4	Zinc sulfate and aluminum hydroxide	9.33	26.03
5	Zinc carbonate basic and aluminum nitrate	0.05 (alkalinity)	21.15
6	Zinc carbonate basic and aluminum hydroxide	0.07 (alkalinity)	24.30
7	Zinc acetate and aluminum nitrate	0.20	22.86
8	Zinc acetate and aluminum hydroxide	0.16	26.25
9	Zinc dust and aluminum hydroxide	0.13	22.70
10	Zinc oxide and aluminum hydroxide	0.11	24.48
	Copper aluminates		
11	Copper nitrate and aluminum nitrate	0.15	29.71
12	Copper nitrate and aluminum hydroxide	0.04 (alkalinity)	34.42
13	Copper sulfate and aluminum nitrate	0.17	24.29
14	Copper sulfate and aluminum hydroxide	0.15	28.61
15	Copper carbonate and aluminum nitrate	0.10	23.96
16	Copper carbonate and aluminum hydroxide	0.06	28.51
17	Copper acetate and aluminum nitrate	0.13	22.32
18	Copper acetate and aluminum hydroxide	0.11	25.56
19	Copper metal and aluminum hydroxide	0.14	26.34
20	Copper oxide and aluminum hydroxide	0.09	29.69

the CuO, ZnO, $CuAl_2O_4$ and $ZnAl_2O_4$ were observed in the samples of copper and zinc aluminates by indicating that the samples were mixed metal oxides. However, the crystalline phases of the CuO, ZnO, $CuAl_2O_4$ and $ZnAl_2O_4$ were pre-dominantly seen in the samples CAnh61, CAnh41, CAnh31, CAnh21, ZAnn61, ZAnn41, ZAnn31 and ZAnn21. However, copper and zinc rich phases in the samples of copper and zinc aluminates were not observed when the samples CAnh11 and ZAnn11 were characterized.

In the Figure 3 (a-b), the XRD patterns of the samples CA61 and ZA61 of the copper and zinc aluminates were given when the samples of zinc and copper aluminates were prepared by solid-solid fusion method by using the different precursors of the zinc, copper and aluminium. The crystalline phases of the CuO, ZnO, $CuAl_2O_4$ and $ZnAl_2O_4$ were pre-dominantly seen in the samples CA61 and ZA61 of zinc and copper aluminates which indicates that the crystalline phases were formed by the solid-solid fusion. However, by using sulphate precursors gave high intensity crystalline phases. The X-ray diffraction is used to explore the phases of the material structures. The XRD patterns of the thermal decomposition of the precursors and solid-solid reactions at 900 ^{o}C in air for 3 h were observed. As reported earlier [37], from the XRD analysis it was shown that if the precursor was heated at temperatures less than 700 °C, a mixture of ZnO and $ZnAl_2O_4$ was obtained. As the temperature was increased from 600 to 700 °C, the XRD patterns of the samples were shown much sharper peaks due to forming the crystalline phases.

In Table 1, the surface areas and alkalinity of the different samples of the copper and zinc aluminates were given. The samples of zinc aluminates prepared by different precursors showed the low surface area, 5.35 to 11.8 $m^2\ g^{-1}$ with low porosity. However, the low acidity of these samples of zinc aluminates was in between 0.22 to 0.58 mmol g^{-1}. The different Zn/Al mole ratios samples ZAnn21, ZAnn31, ZAnn41 and ZAnn61 of zinc aluminates showed the low surface 3.04 to 5.45 $m^2\ g^{-1}$ indicating low porous



(a) (b)

Figure 3. The XRD pattern of the samples. (a). prepared copper aluminates by using different precursors of copper and aluminium with Cu/Al = 6 mole ratio by the solid-solid fusion method and calcined at 900 ^{o}C for 3 h in air; (b) prepared zinc aluminates by using different precursors of zinc and aluminium with Zn/Al = 6 mole

material, and low acidity 0.063 to 0.58 mmol g^{-1}. However, the samples of the copper aluminates, CAnh21, CAnh31, CAnh41 and CAnh61 showed the alkalinity in between 0.04 and 0.21 mmol g^{-1} and also low surface area material. The acidity and alkalinity of the zinc and copper aluminates showed that the different source material used during their preparation has an effect.

In the Figure 4, the FTIR of the samples CA61 and ZA61 of zinc and copper aluminates were given where the samples of zinc and copper aluminates were prepared by different precursors of zinc, copper and aluminium. The FTIR of the samples of zinc and copper aluminates showed that the metal ions zinc, copper and aluminium were bonded through oxygen in the region of wave numbers 450 to 2000 cm^{-1}. However, the hydroxyl or water molecule bonding to the metal ions was observed in the region of wave numbers 3000 to 4000 cm^{-1}. The hydroxyl groups or water molecules helped to capture CO_2 by the samples of zinc and copper aluminates. As reported earlier [37], the IR spectra of the zinc aluminates particles obtained by calcining the precursors at different temperatures, the common peaks were observed in all cases, such as the broad OH peak centered around 3400 cm^{-1} and the H_2O peaks of stretching vibration were at 1380, 1570 cm^{-1}. At the calcinations temperature 900 °C, the peaks below 1000 cm^{-1}, broad peaks around 660 and 530 cm^{-1} were stronger. These bands correspond to the AlO_6 groups, which built up the $ZnAl_2O_4$ spinel [37]. However, the bands correspond to the AlO_6 groups, which built up the $CuAl_2O_4$ or $ZnAl_2O_4$ spinel structures, in the case of copper aluminates, those peaks are stronger.

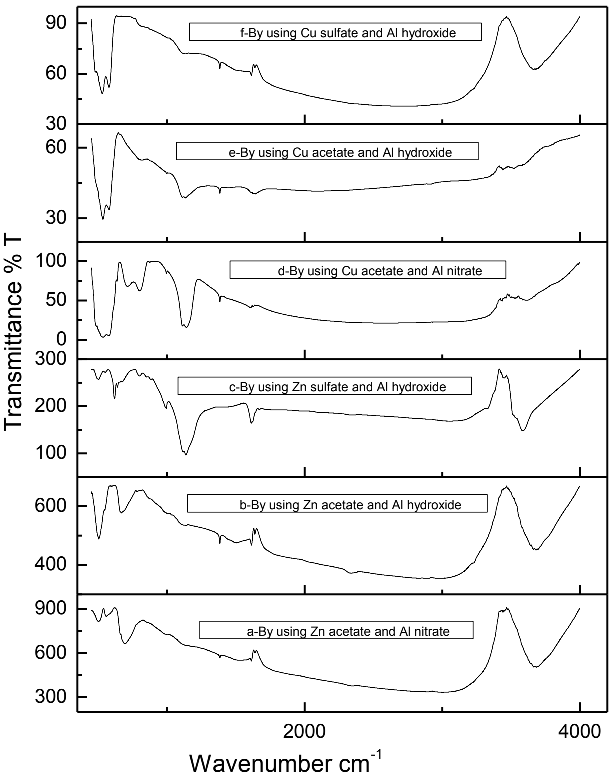


Figure 4. The FTIR of the samples of the zinc and copper aluminates which were prepared by using different precursors of zinc, copper and aluminium

In Figure 5, the SEM images were shown of the samples CAnh61, CAnh41, CAnh31, CAnh21, CAnh11, CAoh61, CAnn61, CAsh61, ZAnn61, ZAnn41, ZAnn31 and ZAnn21, ZAsh61, ZAsn61 and ZAah61, of copper and zinc aluminates. The pre-dominantly formed the crystalline phases of CuO, $CuAl_2O_4$, ZnO and $ZnAl_2O_4$ were observed with the respective mole ratios in the samples of the copper and zinc aluminates. The particles of CuO, $CuAl_2O_4$ ZnO, $ZnAl_2O_4$ and mixed metal oxides were formed separately or aggregation or crystalline forms. The observed particles of CuO, $CuAl_2O_3$, ZnO, $ZnAl_2O_4$ and Al_2O_3 were with uniform crystal size pattern for the different samples prepared by using the different precursors of zinc, copper and aluminium.

In Figure 6, ^{27}Al NMR of the samples CAah61 and ZAah61 of copper, zinc aluminates are shown. The chemical shift of ^{27}Al NMR was very small in zinc aluminates in comparison with that of copper aluminates. The chemical shift of ^{27}Al NMR in the sample of CAah61 was observed at 100 ppm which was indicating that the water molecules or hydroxyl groups are attached to the aluminium ion. The ^{27}Al NMR spectrum of copper aluminate showed a sharp

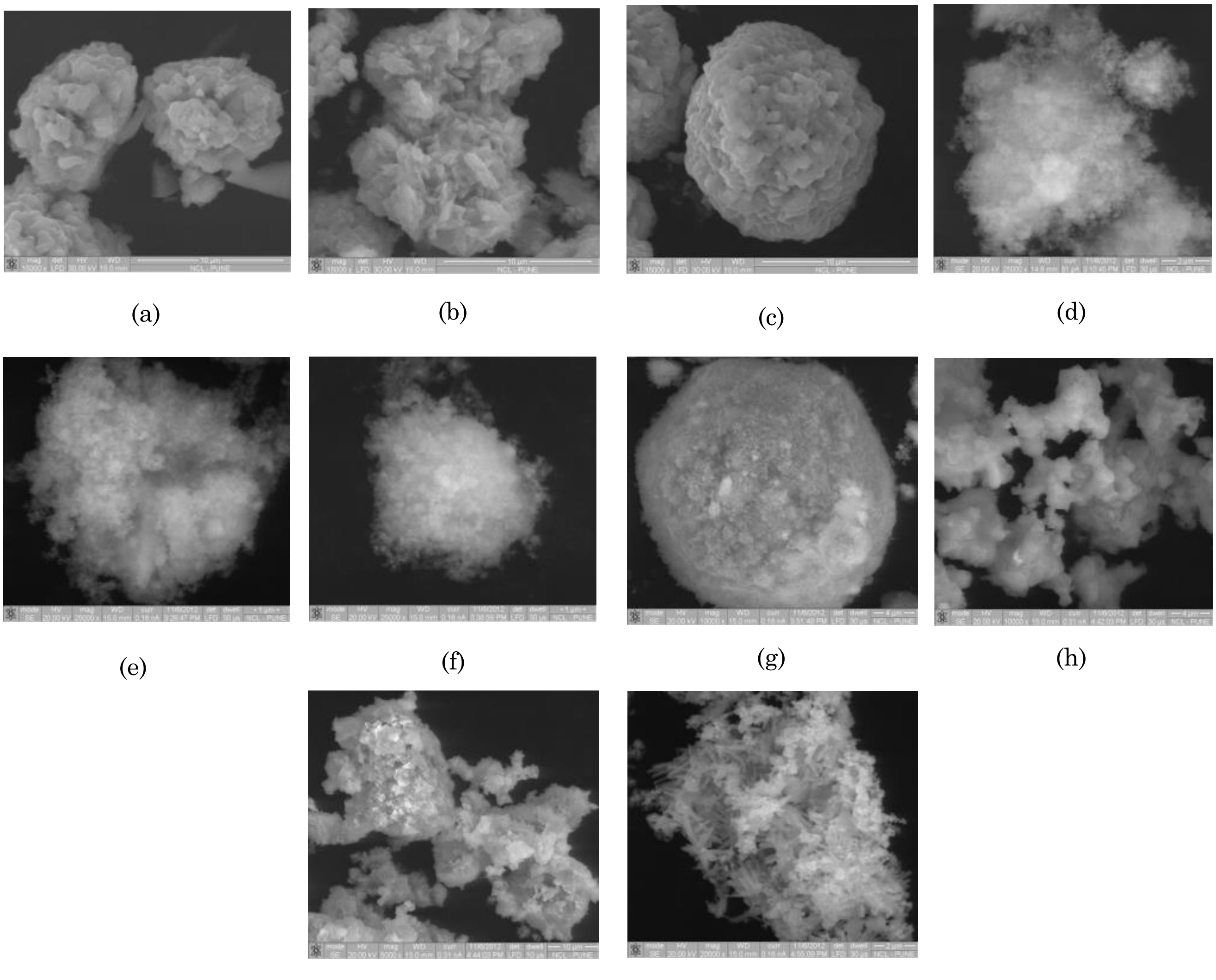
Table 3. The promoter effect on the captured CO_2 at 500 °C by the samples of copper and zinc aluminates with Cu /Al or Zn/Al= 6 mole ratio

Sr. No.	Promoter 2.5 wt% on zinc or copper aluminates	Captured CO_2, wt%
Zinc aluminates with Zn/Al = 6 mole ratio		
1	Li	28.96
2	K	28.29
3	Cs	30.03
4	La	34.78
Copper aluminates Cu/Al = 6 mole ratio		
5	Li	28.75
6	K	28.64
7	Cs	32.91
8	La	33.61

and intense resonance signal at around 0 to 10 ppm characteristic of aluminium in octahedral coordination and one sharp signal at 50 to 70 ppm corresponding to tetrahedrally coordinated aluminium [38]. For the zinc aluminates, ^{27}Al NMR spectroscopy is giving an extremely sensitive probe of the coordination environment of aluminium and can provide an excellent means to investigate the site occupancy of Al^{3+} cations. Al^{3+} (octahedral AlO_6 sites) (chemical shift at 5 ppm) give resonance with chemical shifts in the range -20 to 10 ppm, while those for tetrahedral Al^{3+} centers (tetrahedral AlO_4 sites) (chemical shift at 65 ppm) occur between 50 and 80 ppm. The octahedral peak appears as a doublet. This is a result of a second-order splitting by nuclear quadrupole interactions, which indicates the highly crystalline nature of samples calcined at higher temperatures. The extent of occupancy of tetrahedral sites by Al^{3+} cations showed a marked decrease with calcination temperature. The degree of inversion, calculated from the tetrahedral to octahedral peak area ratio, decreases monotonically with calcinations temperature [39-40].

3.2. The effect of temperature on the captured CO_2

In Figure 7, the effect of temperature on the captured CO_2 by the samples CA21 and ZA61 of copper and zinc aluminates was presented for the temperature 100 to 850 °C. The captured CO_2 by sample of copper and zinc aluminates was observed in the range 18.94 to 25.47 (zinc

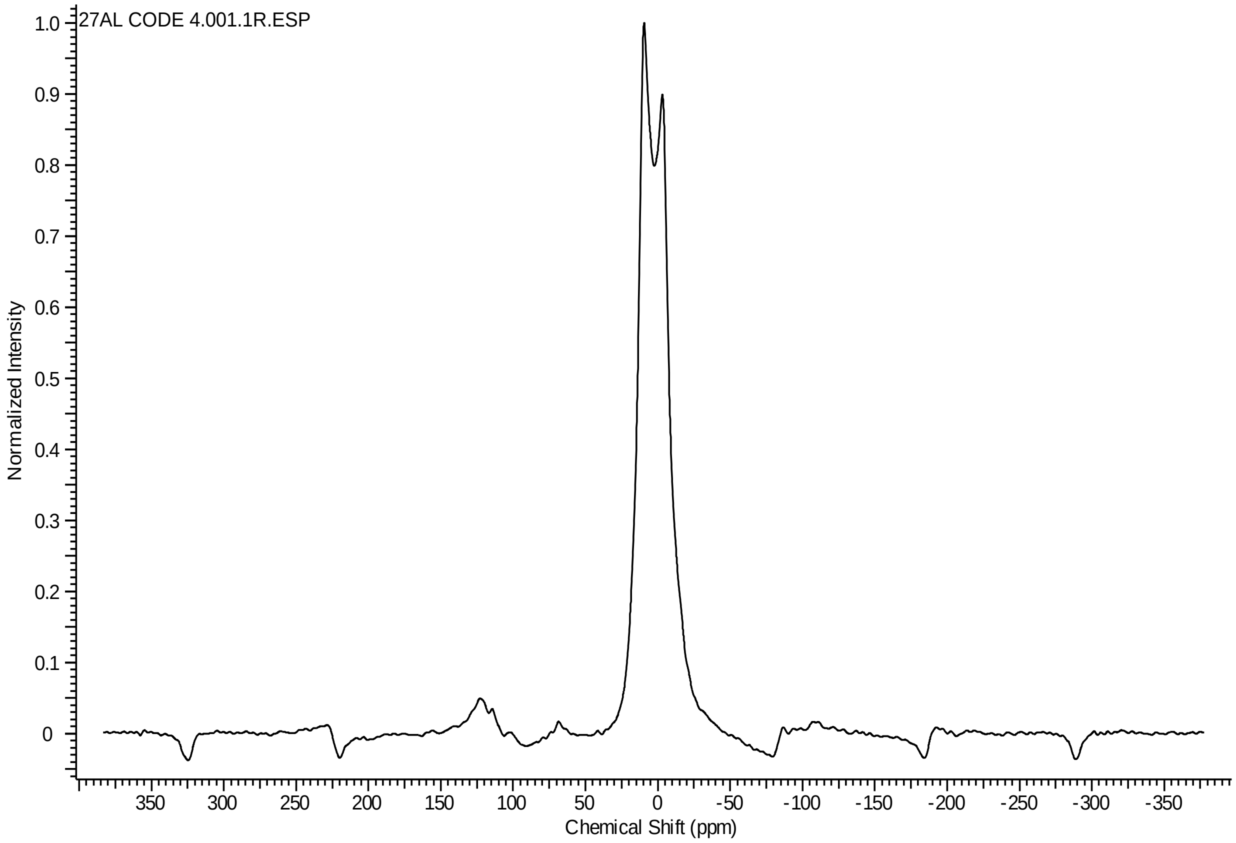


(a) (b) (c) (d)

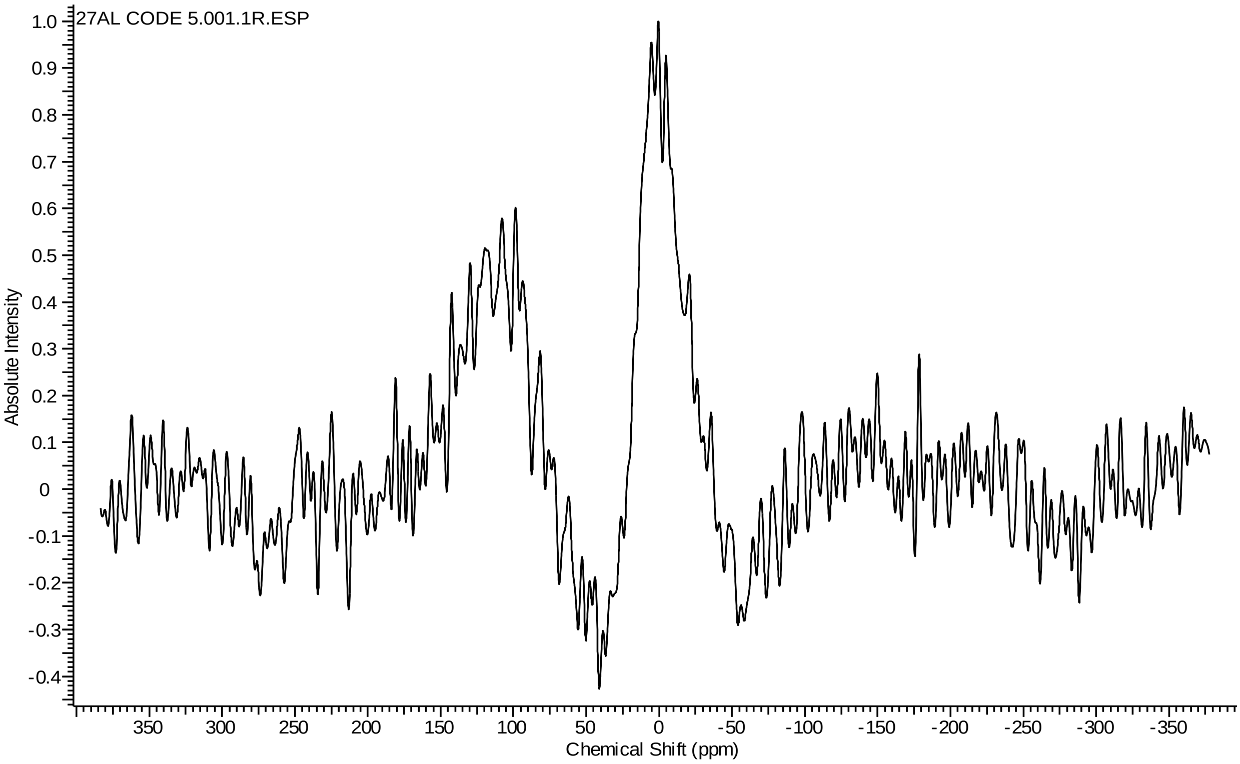
(e) (f) (g) (h)

(i) (j)

Figure 5. The SEM images were given of the samples of copper and zinc aluminates, CA31, CA21, CA11, ZA61, ZA41, ZA31 and ZA21 which were prepared by using the different precursors by solid-solid fusion method. (a) CA11; (b) CA21; (c) CA31; (d) ZA21; (e) ZA31; (f) ZA41; (g) ZA61; (h) ZA61 (from $ZnSO_4$ and $Al(OH)_3$); (i) ZA61 (from $ZnNO_3$ and $Al(NO_3)_3$; (j) ZA61 (from Zinc acetate and $Al(OH)_3$)



(a) ^{27}Al NMR of Zn/Al (6 mole ratio) using Zn acetate and Al hydroxide



(b) ^{27}Al NMR of Cu/Al (6 mole ratio) using Cu acetate and Al hydroxide

Figure 6. The ^{27}Al NMR of the samples. (a) ZAah61 zinc aluminates; (b) CAah61 copper aluminates are shown

aluminates) and 20.36 to 31.32 wt% (copper aluminates). The CO_2 captured by the samples of copper and zinc aluminates was observed in two different temperature zones such as 40 to 400 ^{o}C and 400 to 850 ^{o}C. In the lower temperature zone, copper aluminates had captured higher CO_2 25.25 wt % at 40 ^{o}C, however, zinc aluminates had captured higher CO_2 31.32 wt% at 200 ^{o}C. Moreover, at the higher temperature zone, the captured CO_2 25.73 and 27.42 wt% respectively by the samples of zinc and copper aluminates were higher at the temperature 700 ^{o}C. The captured CO_2 by the sample of copper and zinc aluminates was the formation of copper and zinc carbonate and alumina. The several reactions of carbonate and alumina formation 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, pretreatment and activation temperatures. The hydroxyl groups and water molecules attached to the metal ions could help to capture CO_2. The reversible reactions gave the regenerable adsorbent.

3.3. Effect of different precursors on the captured CO_2 by the samples of zinc and copper aluminates

In Table 2, acidity and the captured CO_2 by the different samples of the zinc and copper aluminates were shown. The captured CO_2 by the samples of zinc aluminates was observed from 21.14 to 26.67 wt%. However, the acidity was 0.09 to 9.37 mmol g^{-1}. The samples of zinc aluminates prepared from zinc carbonate (basic), aluminium nitrate and aluminium hydroxide were found to be 0.05 and 0.07 mmol g^{-1} in alkalinity and showing the captured CO_2 21.14 and 24.4 wt%. The alkalinity and acidity of the samples of zinc and copper aluminates had an effective role on the capturing CO_2. These samples of copper aluminates showed the captured CO_2 24 to 35.16 wt% and acidity in between 0.06 to 0.17 mmol g^{-1}. However, the sample of copper aluminate prepared from copper nitrate and aluminium hydroxide showed the 0.04 mmol g^{-1} alkalinity and captured CO_2 35.16 wt%. The acidity and alkalinity of the zinc and aluminates play the important role for the capturing the CO_2. The hydroxyl groups or water molecules helped to capture CO_2 by the samples of zinc and copper aluminates. The samples of zinc aluminates showed high acidity and low captured CO_2 in comparison with that of the samples of the copper aluminates.

3.3. The effect of Cu: Al and Zn: Al mol ratios on the captured carbon dioxide

In Figure 8, the results of the captured CO_2 at 550 ^{o}C by the samples CAnh61, CAnh41, CAnh31, CAnh21, CAnh11, CAnh0.51 ZAnn61, ZAnn41, ZAnn31 and ZAnn21 of copper and zinc aluminates, were given. The captured CO_2 by the samples CAnh61, CAnh41, CAnh31, CAnh21, CAnh11, ZAnn61, ZAnn41, ZAnn31, ZAnn21 and ZAnn11 of copper and zinc aluminates was observed in the increased mole ratio of Cu/Zn/Al from 0.5 to 6. As the content of the zinc and copper mole ratio in the zinc and copper aluminates increases, the capture of CO_2 by

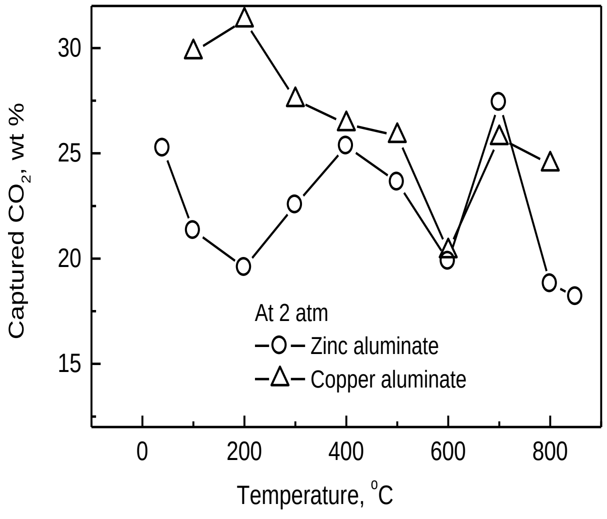


Figure 7. The effect of temperature on the captured CO_2 by the samples of copper and zinc aluminates CA21 and ZA61 were given

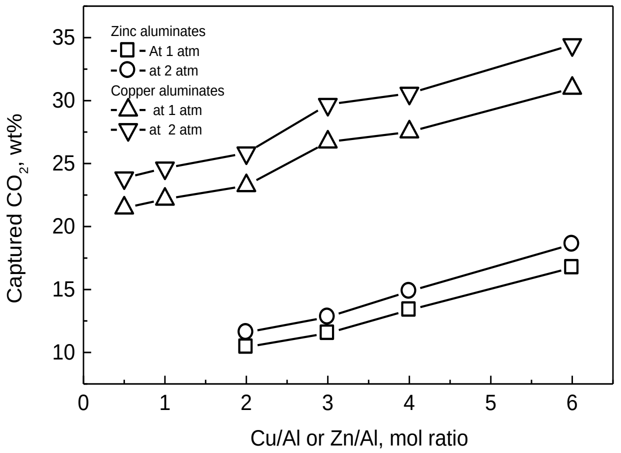


Figure 8. The Effect was illustrated of Zn/Al and Cu/Al mol ratio on the captured CO2 at 550 o C by the samples CA61, CA41, CA31, CA21, CA11, CA0.51 ZA61, ZA41, ZA31 and ZA21 of zinc and copper aluminates

the formation of the zinc and copper carbonate was increased. However, the regeneration of CO_2 from the samples of zinc and copper aluminates and regenerations of zinc and copper aluminates were obtained by increasing the temperature.

3.4. Effect of promoter on the captured CO_2 by the samples of zinc and copper aluminates

In Table 3, the samples of copper and zinc aluminates for the promoter effect were prepared from the copper carbonate, zinc nitrate and aluminium hydroxide by solid-solid fusion method by doping 2.5 wt% each of Li, K, Cs, La and then calcined at 900 ^{0}C for 3 h. The promoters Li, K, Cs and La were tested for the capture of CO_2 at 500 ^{o}C. The promoter effect for the CO_2 capture could be arranged in the increasing order Li<K<Cs<La for the copper and zinc aluminates. Since, the CO_2 is an acidic gas; the addition of alkaline metals also increases the CO_2 capture. However, lanthanum forms the carbonate which also helps to increase the capture of CO_2.

3.5. Effect of carbon dioxide reduction on the CO_2 captured by the samples of copper and zinc aluminates

During the studies of the captured CO_2 by the samples of copper and zinc aluminates, the carbon deposition over the samples of copper and zinc aluminates was noticed for the temperature range from 100 to 900 ^{o}C and also for the different mole ratios of Cu or Zn/Al from 0.5 to 6. These results indicated that the CO_2 was reduced to carbon by the samples of copper and zinc aluminates. The carbon deposition over the copper and zinc aluminates decreased the CO_2 capturing capacity. The carbon dioxide reduction by the samples of zinc aluminates was higher than that of by the samples of copper aluminates. Therefore, the CO_2 captured by the samples of the copper aluminates was higher than that of by the samples of zinc aluminates.

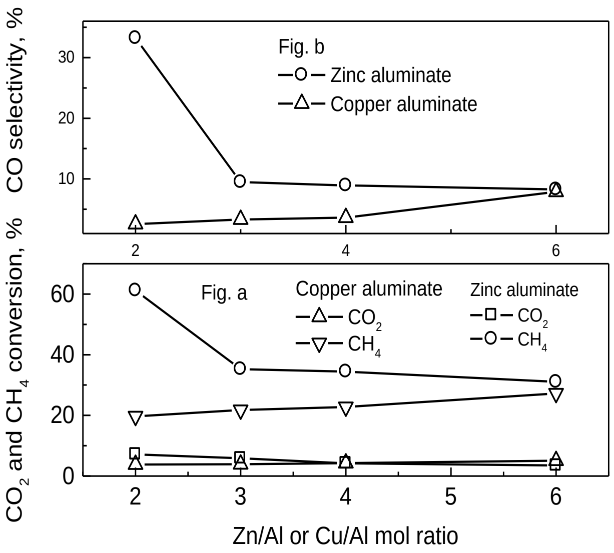


Figure 9. The conversions of CO_2 by methane to syn-gas were given over the samples. (a) CA61, CA41, CA31 and CA21 of the copper aluminates; (b) ZA61, ZA41, ZA31and ZA21 of the zinc aluminates at 500 ^{o}C

3.6. Regeneration of the samples of copper and zinc aluminates for CO_2 capture

Since, the carbon deposition was observed over the copper and zinc aluminates for the range of temperature 100 to 900 ^{o}C, the CO_2 capturing capacity of the samples of copper and zinc aluminates was decreased. Therefore, the regeneration abilities of copper and zinc aluminates were also dropped. There is a need of regeneration of the samples of copper and zinc aluminates by heating in the furnace in presence of air atmosphere at 900 ^{o}C for 3 h.

3.7. The conversion of CO_2 by CH_4 to syn-gas

The catalytic conversion of CO_2 by methane to syn-gas is an endothermic reaction (Equation 14). 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 is supplied to these molecules in the presence of catalyst. Since, the catalytic reaction of CO_2 with methane is endothermic; the reaction was carried out at high temperature. 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, these adsorbent could be, simultaneously, used for the capture of CO_2, and then 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, the high temperature adsorbent for the CO_2 capture could be used for the multipurpose. Moreover, one mole of CO_2 and methane produces the two moles each of CO and H_2.

In Figure 9(a), the conversion of CO_2 by methane over the samples CAnh61, CAnh41, CAnh31, CAnh21, ZAnn61, ZAnn41, ZAnn31 and ZAnn21 with variable mole ratio of copper or zinc with aluminium in the copper and zinc aluminates at 500 °C was explored. The gas hourly space velocities (GHSV = the flow of gas in ml though the catalyst bed per hour and per gram of catalyst) of CO_2, methane and helium, used were constant 12000, 6000 and 1200 ml. $h^{-1}.g^{-1}$. The results of conversion of CO_2 by methane indicate that the conversions of CO_2 and CH_4 show slightly increased with the increased mole ratio of Cu/Al or Zn/Al except the conversion of CH_4 is higher at initial stage in the case of zinc aluminates. With the increase in the mole ratio of Cu/Al or Zn/Al, the mole of Zn or Cu was increased. The increased mole of Cu or Zn contributes to the catalytic reaction. Moreover, there is a carbon deposition over the catalyst which inhibits the reaction. Therefore, either with the increasing in the reaction time or increasing the activity of the catalyst by increasing the mol of Zn or Cu could inhibit the reaction by carbon deposition. During the reaction of CO_2 with methane, the results of analysis of product showed the production of CO and H_2. However, the results were presented of CO selectivity in order to avoid the repetition of the results. The additional product could be carbon and water. Since the temperature was 500 °C, the most of product contains the syn-gas, CO_2 and methane.

$$CO_2 \text{ (high mole ratio)} + CH_4 \text{ (low mole ratio)} \leftrightarrow 2CO + 2H_2 \quad (15)$$

$$CO_2 \text{ (low mole ratio)} + CH_4 \text{ (high mole ratio)} \leftrightarrow 2C + 2H_2O \quad (16)$$

The conversion (from the equations 15 and 16) of CO_2 and CH_4 to syn-gas showed the increased conversion of CO_2 and methane at the low gas hourly space velocity of methane. However, the conversion of CO_2 and methane with the increased in gas hourly space velocity of methane showed the decreased in their values. With the increasing in the gas hourly space velocity of methane (high mole ratio of methane) at the constant gas hourly space velocity of CO_2 (low mole ratio of CO_2), the selectivity of CO and H_2 decreases with the increasing the selectivity of H_2O and carbon (Equation 16). Hence, at low gas hourly space velocity of methane (low mole ratio of methane) and high gas hourly space velocity of CO_2 (high mol ratio of CO_2) the syn-gas formation favours (Equation 15). With the increasing in the gas hourly space velocity of methane (high mole ratio of methane) at the constant gas hourly space velocity of CO_2 (low mole ratio of CO_2), the selectivity of CO and H_2 decreases with the increasing the selectivity of H_2O and carbon (Equation 16). Hence, at low gas hourly space velocity of methane (low mole ratio of methane) and high gas hourly space velocity of CO_2 (high mole ratio of CO_2) the syn-gas formation favours (Equation 15). The mole ratios of CO_2/CH_4 for the conversion of CO_2 by CH_4 could be checked at the level $CO_2/CH_4 = 2$, $CO_2/CH_4 = 1$ and $CO_2/CH_4 = 0.33$. The conversion of CO_2 by CH_4 depends on the CO_2/CH_4 mole ratio, when $CO_2/CH_4 > 1$ mole ratio, then, CO_2 by CH_4 is converted to syn-gas (oxidation process is favourable, where, the CO_2 conversion is comparatively higher than that of CH_4). However, when, $CO_2/CH_4 < 1$ mole ratio, then CO_2 by CH_4 is converted into carbon and water (reduction process is favourable, where, the CO_2 conversion is comparatively lower than that of CH_4). Thus, CO_2/CH_4 mole ratio is an important factor for achieving the desired product. When $CO_2/CH_4 > 1$ mole ratio, then, CO_2 conversion is higher in comparison with that of CH_4. Moreover, $CO_2/CH_4 < 1$ mole ratio, then CH_4 conversion is higher in comparison with that of CO_2. Thus, the under the extreme conditions of mole ratios of $CO_2/CH_4 >>> 1$, the oxygenated product of CH_4 and CO_2 could be possible. However, in the other side, when mole ratios of $CO_2/CH_4 <<< 1$, then the hydrogenated product of CO_2 and methane could be possible.

From Figure 9 (b), the selectivity to CO from the conversion of CO_2 and CH_4 was higher in the initial stage in the case of zinc aluminates. However, the CO selectivity was increased from 2.55 to 7.89 % for 2 to 6 mole ratio of Cu/Al in the copper aluminates.

In Table 4, at the mole ratio of CO_2 to methane 61.27, the conversion of CO_2 by methane was studied over the samples CAnh61 and ZAnn61 of zinc and copper aluminates. The results of conversion of CO_2 by CH_4 to syn-gas were studied by analysing the samples of product with respective reaction time. The conversion of CO_2 and methane was decreased with respective time 7.28 to 5.95 % and 24.43 to 1.18, respectively in the case of zinc aluminates. However, CO selectivity was decreased from 52.63 to 6.13. Moreover, in the case of copper (II) aluminates, CO_2 conversion was decreased with respective time from 8.04 to 7.27 % while methane conversion was increased from 2.96 to 7.37 %. The CO selectivity was dropped from 14.67 to 13.30 %. The similar trend of conversion of CO_2 and CH_4 and selectivity to CO was observed in the case of copper (I) aluminates.

Table 4. The conversion of CO_2 by methane to syn-gas over copper and zinc aluminates at CO_2/CH_4 = 61.37 mole ratio and 500 °C reaction temperature

Sr. No	Reaction time, min	CO_2 conversion,%	CH_4 conversion,%	CO selectivity,%
		Zinc aluminate with Zn/Al = 6 mole ratio		
1	5	7.28	24.43	52.63
2	20	6.73	2.82	9.05
3	30	5.93	1.18	6.13
		Copper (II) aluminate with Cu/Al = 6 mole ratio		
4	5	8.04	2.96	14.67
5	20	7.45	5.11	11.81
6	30	7.27	7.37	11.30
		Copper (I) aluminate with Cu/Al = 2 mole ratio		
7	5	7.19	6.00	12.64
8	20	6.69	18.85	11.30
9	30	6.14	20.32	11.07

Table 5. The conversion of CO_2 by methane to syn-gas over copper and zinc aluminates at CO_2/CH_4 = 0.057 mole ratio and 500 °C reaction temperature

Sr. No	Reaction time, min	CO_2 conversion,%	CH_4 conversion,%	CO selectivity,%
		Zinc aluminate with Zn/Al = 6 mole ratio		
1	5	21.43	7.15	0.61
2	20	15.19	7.60	0.21
3	30	14.86	7.75	0.17
		Copper (II) aluminate with Cu/Al = 6 mol ratio		
4	5	5.78	9.79	0.36
5	20	12.56	7.98	0.15
6	30	12.75	7.13	0.14
		Copper (I) aluminate with Cu/Al = 2 mol ratio		
7	5	10.12	8.39	0.18
8	20	14.73	8.21	0.10
9	30	17.62	7.79	0.094

In Table 5, at the mole ratio of CO_2 to methane 0.057, the conversion of CO_2 by methane was studied over the samples CAnh61 and ZAnn61 of zinc and copper aluminates. The results of conversion of CO_2 by CH_4 to syn-gas were studied by analysing the samples of product with respective reaction time. The conversion of CO_2 was decreased with respective time 21.43 to 14.86 % in the case of zinc aluminates. The conversion of methane was increased from 7.15 to 7.75 %. However, CO selectivity was decreased from 0.61 to 0.17. Moreover, in the case of copper(II) aluminates, CO_2 conversion was increased with respective time from 5.78 to 12.75 % where the methane conversion was decreased from 9.79 to 7.13 %. The CO selectivity was dropped from 0.36 to 0.14%. The similar nature of conversion of CO_2 and CH4 and selectivity to CO was observed in the case of copper (I) aluminates.

4. Conclusions

The different samples of the copper and zinc aluminates were prepared by solid-solid fusion method. The samples of copper and zinc aluminates were characterized for acidity/alkalinity, surface area, XRD patterns, FTIR and SEM images. The correlation between the acidity/ alkalinity and captured CO_2 by the samples of the copper and zinc aluminates showed the increased CO_2 with decreased acidity of the copper and zinc aluminates. The captured CO_2 by the samples of copper and zinc aluminates was the formation of copper and zinc carbonates and alumina. 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 application. The hydroxyl groups or water molecules helped to capture CO_2 by the samples of zinc and copper aluminates. The reversible reactions gave the regenerable adsorbent. The conversion of CO_2 by methane over the samples of copper and zinc aluminates at 500 ^oC produced the syn-gas. Thus, the CO_2 adsorbents could be used to produce syn-gas by the reaction of CO_2 with methane.

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