

Synthesis and Characterization of Calcium Aluminate Spinel Using Solution Combustion Method

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Abstract— In this paper the Calcium aluminate nanoparticles were prepared by solution combustion method, using procured calcium nitrate, aluminium nitrate and urea (as fuel). Stoichiometric amounts of calcium nitrate, aluminium nitrate, and fuel urea were calculated using the total oxidizing and reducing valencies of the compounds which serve as numerical coefficients for stoichiometric balance. Initially $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved in a minimum quantity of water along with urea in a silica crucible (with a volume of 100cm^3). The crucible was introduced into the muffle furnace which was preheated to 500°C . Also the variation of fuel to oxidizer (F/O) ratio was studied. The study was carried out for leaner to richer fuel ratios. In the case of CaAl_2O_4 combustion synthesis results were achieved when fuel (urea) was used. The use of fuel allowed the formation of pure, nano-crystalline CaAl_2O_4 directly from the combustion reaction. The effect of fuel ratios was investigated by variation of the ratios in which the fuel was taken.

Key words: Muffle furnace, solution combustion synthesis, CaAl_2O_4 Spinel, XRay-diffraction, SEM

I. INTRODUCTION

Calcium aluminate has been long involved in the practical applications in the cement and concrete industry, as well as in refractories and ceramic materials. Recently new advanced applications of calcium aluminate have appeared in optical and structural ceramics. Calcium aluminates (CA) are widely used in the steel and cement industry due to their relatively low density, hardness, straightness, etc. They are important constituents for refractory castables and govern their applicability to the service temperature. Calcium aluminate (CaAl_2O_4) has received considerable attention as a material for (implants) bone graft application due to its unique combination of physical and mechanical, bioactive and biocompatible properties. Also, CA-based glasses have technological importance in application of optical devices. Various synthesis methods have been developed to obtain CA with controlled particle size.

Traditionally calcium aluminate is produced by solid state reactions. The main drawback of this method is the required high temperature and the presence of multiple and not desired phases with the end product. Other methods are developed also using high temperatures. In order to synthesize mono-phase calcium aluminate, a long treatment period is required which leads to decreasing of surface area of product.

Park and Kim Referred to use boric acid as a flux to accelerate the formation of the product by solid state reactions of CaO and Al_2O_3 powders. The molten flux leads to uniform distribution of compounds and

enhances diffusion of the precursors. This method enables to decrease the synthesis temperature. Many approaches are suggested to increase homogeneity of the precursors. Among them is sol-gel method. In this case precursors containing gel are prepared firstly. Later on, the gel is crystallized by subsequent heating at relatively low temperature. The most obvious advantage of the sol-gel method is that reagents are mostly mixed in atomic level, which may increase the reaction rate and decrease the synthesis temperature.

Douy and Gervais Referred a synthesis method of amorphous CaAl_2O_4 powders by spray-drying aqueous solutions of calcium and aluminum nitrates, followed by calcinations of product in order to completely decompose the salts. One of the well-known approaches of ceramic powder synthesis is Pechini method. The process is based on the ability of certain organic acids to chelate the metal ion. Heating the chelates, polyesterification undergoes with the help of polyhydroxy alcohols and polymerized the resin forms. Then, the polymerized resin is calcined to obtain calcium aluminate. Also using chemical fixation of the cations by organic molecules Pati et al. and Gaki et al. have obtained nanoparticles of CaAl_2O_4 by versatile solution based precursor solution method.

The combustion method is a convenient method for the synthesis of oxide materials. It is a versatile, simple and rapid process, which allows to synthesize variety of materials without intermediate decomposition steps. This is a self-sustaining process and it is ignited in a temperature which is much lower than the actual phase transformation temperature. The calcium monoaluminate (CaAl_2O_4) has been synthesized with high purity via solution combustion methods, using aqueous solution of calcium and aluminium nitrates as both oxidizer and source of the corresponding cations and urea as a fuel. However, obtained products are mainly agglomerated, nevertheless this method do not need high temperatures as other methods.

The objective of this work is to study the influence of the quantity of urea on the possibility of synthesizing of calcium aluminate by the solution combustion synthesis method, using calcium and aluminum nitrites as precursors.

II. EXPERIMENTAL PROCEDURE

A. Synthesis of CaAl_2O_4 nanoparticle

The Calcium aluminate Nano powder were prepared by solution combustion method, using procured calcium nitrate, aluminium nitrate and urea (as fuel). Stoichiometric amounts of calcium nitrate, aluminium nitrate, and fuel urea were calculated using the total oxidizing and reducing valencies of the compounds which

serve as numerical coefficients for stoichiometric balance. Initially $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved in a minimum quantity of water along with urea in a crucible (with a volume of 100cm^3). The crucible was introduced into the muffle furnace which was preheated to 500°C .



Fig. 1: Muffle furnace



Fig. 2: Crucible inside the muffle Furnace

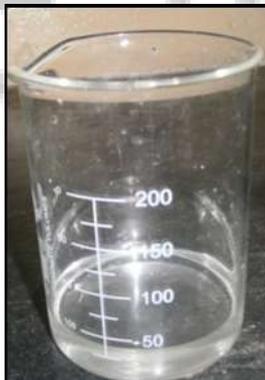
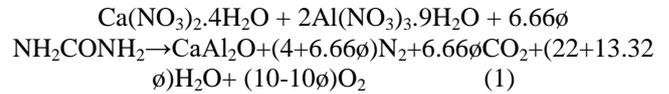


Fig. 3: Clear solution in crucible

B. Solution Combustion Synthesis (SCS) of Calcium Aluminate (CaAl_2O_4) with Fuel to Oxidizers Ratios:

Calcium Nitrate, Aluminum Nitrate, ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) and urea ($\text{CO}(\text{NH}_2)_2$), were used as oxidizer and fuel respectively for solution combustion synthesis. These reactants are mixed in the required molar ratios with required amount in a minimum volume of deionized water to obtain clear aqueous solutions. The solution is kept in furnace preheated to 500°C . First thermal dehydration (at 100°C) takes place forming viscous solution, at 200°C the viscous liquids swelled and gets auto ignited, with the rapid evolution of a large volume of gases to produce voluminous powders. The nature of ignition depended on the fuel-to-oxidant ratio. The auto ignition of the precursor containing

fuel-to-oxidant ratio according to the concept of propellant chemistry and fuel rich ratio was found to be more violent compared to the fuel-deficient precursor. Because the time for which the auto ignition exists is rather small (typically 5 s), under the equilibrium conditions the standard reaction equation in this systems can be represented for all trivalent nitrates - urea combustion (Where M =trivalent cation) for fuel to oxidizer ratio as For all Calcium nitrate, Aluminium nitrate, urea, combustion for F/O ratios equation can be written as.



Here the ϕ is the fuel to oxidizer equivalence ratio (not the urea to nitrate molar ratio) given by the formula

$$\frac{\text{Fuel}}{\text{Oxidiser}} \text{ Ratio} = \frac{\sum \text{all oxidising and reducing elements in fuel}}{\sum \text{all oxidising and reducing elements in oxidizer}}$$



Fig. 4: Different powders formed after SCS with fuel to oxidizer (F/O) variation when urea was used as fuel.



Fig. 5. a) No flame is formed when the F/O=0.4 inside the muffle furnace



Fig. 5. b) No flame is formed when the F/O=0.8 inside the muffle furnace



Fig. 5.c) flame is formed when the F/O=1 inside the muffle furnace



Fig. 5.d) flame is formed when the F/O=1.2 inside the muffle furnace



Fig. 5.e) flame is formed when the F/O=1.4 inside the muffle furnace



Fig. 5. f) flame is formed when the F/O=1.6 inside the muffle furnace

C. Structural, Compositional and Micro-structural Analysis.

1) X-ray diffraction (XRD)

X-ray diffraction studies were carried out for phase confirmation and calculating crystallite size of the milled samples, using D8-Advance-Bruker machine with Cu-K_α (wavelength of Cu-K_α (λ) ~1.5406 Å) radiations for all the measurements. Ni filter was used to attenuate K_β lines. The crystallite size of powders was calculated using Scherrer's

formula where an assumption was made that the particle is spherical in shape. The Scherrer's formula gives

$$\beta_{\theta} = \frac{K \cdot \lambda}{L \cdot \cos \theta} \quad (2)$$

where, β_{θ} is the full width at half maximum (FWHM) of diffracted peaks in degrees, L stands for the liner dimension of particles in meters, θ refers to Bragg's angle in degrees and K' is the shape factor, generally known as a numerical constant and evaluated as 0.93 and depends on shape of crystallites. From this expression, it is clearly seen that diffracted beam gets broadened as the size of crystallite reduces. Silicon was used as an external standard for correction due to instrumental broadening. The XRD Machine is shown in Figure 6.



Fig. 6: XRD Machine

2) Scanning electron microscope (SEM)

The surface morphology of powders and pellet samples was studied using scanning electron microscope a Cambridge, stereoscan-240. (ESEM -FEI, Quanta 200) and elemental compositional analysis was done using the attached energy dispersed analysis of X-rays (EDAX). The grain size of the chosen materials was seen clearly using FEG-SEM since it produces the primarily high electron brightness at low accelerating potentials. All the samples studied were ceramic oxide insulator materials (non conductors), the gold coating was done to avoid the charge accumulation on sample surface by making path way to the ground. Grain size was estimated using linear intercept method. The scanning Electron Microscope(SEM) is as shown in figure 7.



Fig. 7: SEM

D. Thermodynamic Modeling

For comparing exothermicity of fuel in reaction with the nitrates, enthalpy and adiabatic flame temperature of the

reactions between urea and aluminum nitrate were calculated in the conditions Stoichiometric, Fuel lean and Fuel rich. Using the thermodynamic data for the various reactants and products listed in Table 1, the enthalpy of combustion and the theoretical adiabatic flame temperatures as a function of F/O ratio were approximately calculated by the following equations: using Mathematical software.

$$\Delta H^{\circ} = (\sum n\Delta H^{\circ})_{\text{products}} - (\sum n\Delta H^{\circ})_{\text{reactant}} \quad (3)$$

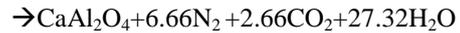
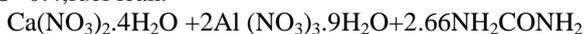
compound	ΔH_f (kcal.mol ⁻¹)	c_p (cal.mol ⁻¹ .K ⁻¹)
CaAl ₂ O ₄	-534	42.79
Al(NO ₃) ₃ .(c)	-857.59	-
Zn(NO ₃) ₂ .6H ₂ O (c)	-551.30	-
NH ₂ CONH ₂ (c)	-79.71	-
NH ₂ CH ₂ COOH (c)	-126.22	-
CH ₃ CHNH ₂ CO OH (c)	-	-
Ca (NO ₃) ₂ .4H ₂ O (c)	-100.26 -509.64	- -
Mg	-624.59	-
(NO ₃) ₃ .6H ₂ O (c)	-217.75	-
SiO ₂	-70.52	-
C ₂ H ₆ N ₄ O ₂ (ODH)	-28.8 -764.447	- 52.3+ 0.00774T
C ₆ H ₁₂ N ₄ (HMT)	-87.37	33.3
CaMgSi ₂ O ₆ (c)	-399.09	22.08 + 0.0089T
NH ₄ NO ₃ Al ₂ O ₃ (c)	-	-
ZnO (c)	-83.24	11.40 + 0.00145T - 182400/T ²
CO ₂ (g)	-94.051	10.34 + 0.00274T - 195500/T ²
NO ₂ (g)	7.93	8.8
N ₂ (g)	0	6.50 + 0.0010T
H ₂ O (g)	-57.796	8.22 + 0.00015T + 0.00000134T ²
H ₂ O (l)	-68.38	-
O ₂ (g)	0	8.27 + 0.000258T - 18770/T ²
C (c)	0	2.673 + 0.002617T - 116900/T ²
C(carbon)	0	2.038
HCNO(g)	40.88	11.21
NH ₃ (g)	-10.96	-
N ₂ O(g)	19.5	-

Table 1: Relevant thermodynamics data of reactants and products

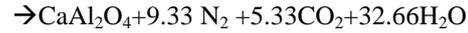
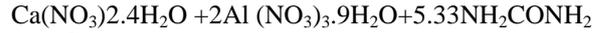
III. RESULTS AND DISCUSSION

Solution Combustion Synthesis (SCS) of Calcium Aluminate (CaAl₂O₄) with Various F/O Ratios:

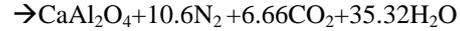
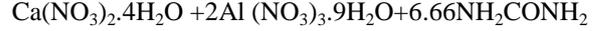
Considering the reaction of nitrates with the urea fuel the obtained results are, For fuel lean $\phi < 1$, three compositions of fuel lean are $\phi = 0.4, 0.8$ and chemical equations are respectively (60%, 20% fuel lean) $\phi = 0.4$, fuel lean.



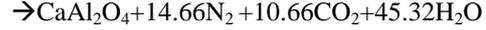
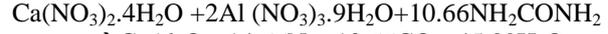
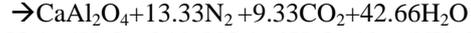
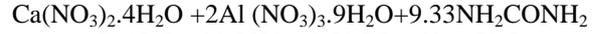
$\phi = 0.8$, fuel lean



Fuel stoichiometric ratio $\phi = 1$



Fuel rich $\phi > 1$ $\phi = 1.2, 1.4, 1.6$ (20%, 40%, 60% fuel rich) reaction equations are

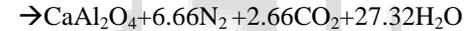
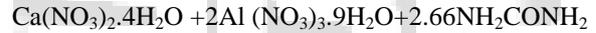


SNo	Fuel/oxidizer ratio	Urea-to-nitrate molar ratio	Ca(NO ₃) ₂ .4H ₂ O grams	Al(NO ₃) ₃ .9H ₂ O gram	CO(NH ₂) ₂ gram	Reaction type	Foam nature Colour of the powder
01	0.4	1	4.78	15	3.2	NO flame	White
02	0.8	1.5	4.78	15	6.4	NO flame	White
03	1.0	2.5	4.78	15	8	Flame	White
04	1.2	3.0	4.78	15	9.6	Flame	White
06	1.4	3.5	4.78	15	11.20	Flame	White
07	1.6	4	4.78	15	12.8	Flame	White

Table 2. Amount of fuel and oxidizer, Physical characteristics of the combustion reaction for different Urea-to-nitrate ratios (Fuel- oxidizer ratios)

A. Adiabatic Flame Temperature and Enthalpy Calculations for Urea as Fuel

1) $\phi = 0.4$, fuel lean.



$$\Delta H_{\text{(Products)}} = \Delta H_{\text{(CaAl}_2\text{O}_4)} + 6.66 \Delta H_{\text{(N}_2)} + 2.66 \Delta H_{\text{(CO}_2)} + 27.32 \Delta H_{\text{(H}_2\text{O)}}$$

$$\Delta H_{\text{(Products)}} = -534 + 6.66 \cdot 0 + 2.66 \cdot (-94.051) + 27.32 \cdot (-57.796) = -2363.15 \text{ kcal mol}^{-1}$$

$$\Delta H_{\text{(Reactants)}} = \Delta H_{\text{(Ca(NO}_3)_2 \cdot 4\text{H}_2\text{O)}} + 2 \Delta H_{\text{(Al(NO}_3)_3 \cdot 9\text{H}_2\text{O)}} + 2.66 \Delta H_{\text{(NH}_2\text{CONH}_2)}$$

$$\Delta H_{\text{(Reactants)}} = -509.64 + 2 \cdot (-857.59) + 2.66 \cdot (-79.71) = -2436.20 \text{ kcal mol}^{-1}$$

$$\Delta H_{\text{(Reaction)}} = \Delta H_{\text{(Products)}} - \Delta H_{\text{(Reactants)}}$$

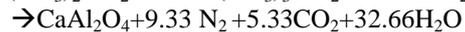
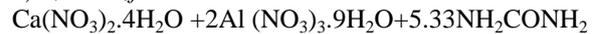
$$\Delta H_{\text{(Reaction)}} = -2363.15 - (-2436.20) = 73.05 \text{ kcal mol}^{-1}$$

$$C_p = 42.79 + 6.66 \cdot 6.961 + 2.66 \cdot 8.87 + 27.32 \cdot 8.025 = 331.22 \text{ cal mol}^{-1}$$

$$T_{\text{ad}} = T_0 + (\Delta H_p - \Delta H_r) / C_p$$

$$= 298 + (73.05 / 331.22) \times 1000 = 518.54$$

2) $\phi = 0.8$, fuel lean



$$\Delta H_{\text{(Products)}} = \Delta H_{\text{(CaAl}_2\text{O}_4)} + 9.33 \Delta H_{\text{(N}_2)} + 5.33 \Delta H_{\text{(CO}_2)} + 32.66 \Delta H_{\text{(H}_2\text{O)}}$$

$$\Delta H_{\text{(Products)}} = -534 + 9.33 \cdot 0 + 5.33 \cdot (-94.051) + 32.66 \cdot (-57.796) = -2922.9 \text{ kcal mol}^{-1}$$

$$(-57.796) = -2922.9 \text{ kcal mol}^{-1}$$

$$\Delta H_{\text{(Reactants)}} = \Delta H_{\text{(Ca(NO}_3)_2 \cdot 4\text{H}_2\text{O)}} + 2 \Delta H_{\text{(Al(NO}_3)_3 \cdot 9\text{H}_2\text{O)}} + 5.33 \Delta H_{\text{(NH}_2\text{CONH}_2)}$$

$$\Delta H_{\text{(Reactants)}} = -509.64 + 2 \cdot (-857.59) + 5.33 \cdot (-79.71) = -2649.59 \text{ kcal mol}^{-1}$$

$$\Delta H_{\text{(Reaction)}} = \Delta H_{\text{(Products)}} - \Delta H_{\text{(Reactants)}}$$

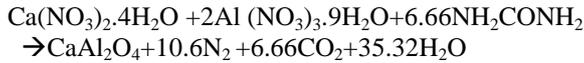
$$\Delta H_{\text{(Reaction)}} = -2922.9 - (-2649.59) = -273 \text{ kcal mol}^{-1}$$

$$C_p = 42.79 + 9.33 \times 6.961 + 5.33 \times 8.87 + 32.66 \times 8.025 = 418.40 \text{ cal mol}^{-1}$$

$$T_{ad} = T_o + (\Delta H_p - \Delta H_r) / C_p$$

$$= 298 + (273 / 418.4) \times 1000 = 950.48$$

3) Fuel stoichiometric ratio $\phi = 1$



$$\Delta H_{(\text{Products})} = \Delta H_{(\text{CaAl}_2\text{O}_3)} + 10.6 * \Delta H_{(\text{N}_2)} + 6.6$$

$$* \Delta H_{\text{CO}_2} + 35.32 * \Delta H_{\text{H}_2\text{O}}$$

$$\Delta H_{(\text{Products})} = -534 + 10.6 * 0 + 6.66 * (-94.051) + 35.32 * (-57.796) = -3201.72 \text{ kcal mol}^{-1}$$

$$\Delta H_{(\text{Reactants})} = \Delta H_{(\text{Ca}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O})} + 2 * \Delta H_{(\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O})} + 6.6 * \Delta H_{(\text{NH}_2\text{CONH}_2)}$$

$$\Delta H_{(\text{Reactants})} = -509.64 + 2 * (-857.59) + 6.6 * (-79.71) = -2755.66 \text{ kcal mol}^{-1}$$

$$\Delta H_{(\text{Reaction})} = \Delta H_{(\text{Products})} - \Delta H_{(\text{Reactants})}$$

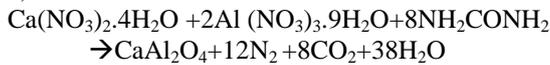
$$\Delta H_{(\text{Reaction})} = -3201.72 - (-2755.66) = -446.06 \text{ kcal mol}^{-1}$$

$$C_p = 42.79 + 10.6 \times 6.961 + 6.66 \times 8.87 + 35.32 \times 8.025 = 433.39 \text{ cal mol}^{-1}$$

$$T_{ad} = T_o + (\Delta H_p - \Delta H_r) / C_p$$

$$= 298 + 446.06 / 433.39 \times 1000 = 1327.23$$

4) Fuel stoichiometric ratio $\phi = 1.2$



$$\Delta H_{(\text{Products})} = \Delta H_{(\text{CaAl}_2\text{O}_3)} + 12 * \Delta H_{(\text{N}_2)} + 8 * \Delta H_{\text{CO}_2} + 40 * \Delta H_{\text{H}_2\text{O}}$$

$$\Delta H_{(\text{Products})} = -534 + 12 * 0 + 8 * (-94.051) + 40 * (-57.796) = -3482.24 \text{ kcal mol}^{-1}$$

$$\Delta H_{(\text{Reactants})} = \Delta H_{(\text{Ca}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O})} + 2 * \Delta H_{(\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O})} + 8 * \Delta H_{(\text{NH}_2\text{CONH}_2)}$$

$$\Delta H_{(\text{Reactants})} = -509.64 + 2 * (-857.59) + 8 * (-79.71) = -2862.5 \text{ kcal mol}^{-1}$$

$$\Delta H_{(\text{Reaction})} = \Delta H_{(\text{Products})} - \Delta H_{(\text{Reactants})}$$

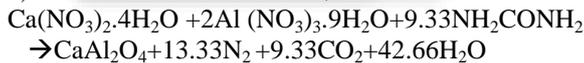
$$\Delta H_{(\text{Reaction})} = -3482.24 - (-2862.24) = -619.74 \text{ kcal mol}^{-1}$$

$$C_p = 42.79 + 12 \times 6.961 + 8 \times 8.87 + 38 \times 8.025 = 501.62 \text{ cal mol}^{-1}$$

$$T_{ad} = T_o + (\Delta H_p - \Delta H_r) / C_p$$

$$= 298 + (619.74 / 501.62) \times 1000 = 1533.73$$

5) Fuel stoichiometric ratio $\phi = 1.4$



$$\Delta H_{(\text{Products})} = \Delta H_{(\text{CaAl}_2\text{O}_3)} + 13.33 * \Delta H_{(\text{N}_2)} + 9.33 * \Delta H_{\text{CO}_2} + 40.66 * \Delta H_{\text{H}_2\text{O}}$$

$$\Delta H_{(\text{Products})} = -534 + 13.33 * 0 + 9.33 * (-94.051) + 40.66 * (-57.796) = -3761.47 \text{ kcal mol}^{-1}$$

$$\Delta H_{(\text{Reactants})} = \Delta H_{(\text{Ca}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O})} + 2 * \Delta H_{(\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O})} + 9.33 * \Delta H_{(\text{NH}_2\text{CONH}_2)}$$

$$\Delta H_{(\text{Reactants})} = -509.64 + 2 * (-857.59) + 9.33 * (-79.71) = -2968.51 \text{ kcal mol}^{-1}$$

$$\Delta H_{(\text{Reaction})} = \Delta H_{(\text{Products})} - \Delta H_{(\text{Reactants})}$$

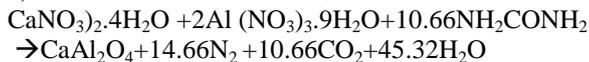
$$\Delta H_{(\text{Reaction})} = -3761.47 - (-2968.51) = -792 \text{ kcal mol}^{-1}$$

$$C_p = 42.79 + 13.33 \times 6.961 + 9.33 \times 8.87 + 40.66 \times 8.025 = 549.15 \text{ cal mol}^{-1}$$

$$T_{ad} = T_o + (\Delta H_p - \Delta H_r) / C_p$$

$$= 298 + (792.96 / 549.97) \times 1000 = 1741.97$$

6) Fuel stoichiometric ratio $\phi = 1.6$



$$\Delta H_{(\text{Products})} = \Delta H_{(\text{MgAl}_2\text{O}_3)} + 14.66 * \Delta H_{(\text{N}_2)} + 10.66 * \Delta H_{\text{CO}_2} + 43.32 * \Delta H_{\text{H}_2\text{O}}$$

$$\Delta H_{(\text{Products})} = -534 + 14.66 * 0 + 10.66 * (-94.051) + 45.32 * (-57.796) = -4039.72 \text{ kcal mol}^{-1}$$

$$\Delta H_{(\text{Reactants})} = \Delta H_{(\text{Ca}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O})} + 2 * \Delta H_{(\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O})} + 10.66 * \Delta H_{(\text{NH}_2\text{CONH}_2)}$$

$$\Delta H_{(\text{Reactants})} = -509.64 + 2 * (-857.59) + 10.66 * (-79.71) = -3074.52 \text{ kcal mol}^{-1}$$

$$\Delta H_{(\text{Reaction})} = \Delta H_{(\text{Products})} - \Delta H_{(\text{Reactants})}$$

$$\Delta H_{(\text{Reaction})} = -4039.72 - (-3074.52) = -965.20 \text{ kcal mol}^{-1}$$

$$C_p = 42.79 + 14.66 \times 6.961 + 10.66 \times 8.87 + 43.32 \times 8.025 = 586.28 \text{ cal mol}^{-1}$$

$$T_{ad} = T_o + (\Delta H_p - \Delta H_r) / C_p$$

$$= 298 + (965.20 / 586.28) \times 1000 = 1944.33$$

Complete combustion					
S No	F/O ratio ϕ	Urea/nitrate molar ratio	Enthalpy Kcal/mol	Adiabatic flame Temp C At 500°C	No gases evolved
1	0.4	0.5	73.05	518.54	46.5
2	0.8	1	-273	9504.8	57.5
3	1.0	1.5	-446.06	1327.23	62.5
4	1.2	2	-619.74	1533.73	67.5
5	1.4	2.5	-792.96	1741.97	75
6	1.6	3	-965.20	1944.33	79.5

Table: 3 Effect of Urea – Nitrate F/O ratio on adiabatic flame temperature, enthalpy of reaction, no of moles of gases evolved

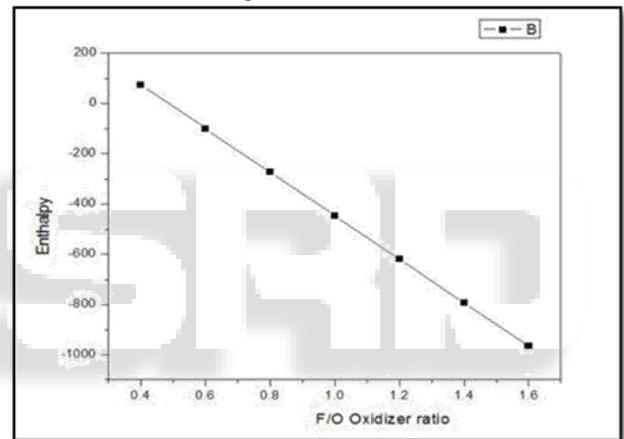


Fig. 8: Graph representing the enthalpy vs F/O ratio For urea as a fuel

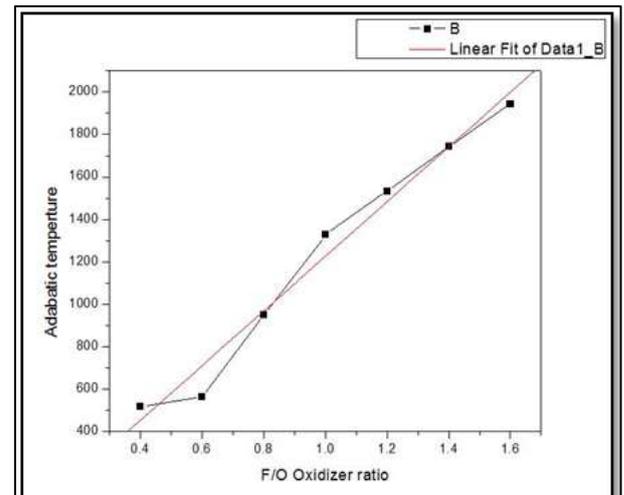


Fig. 9: Graph representing the Adiabatic temperature v/s F/O ratio For urea as a fuel

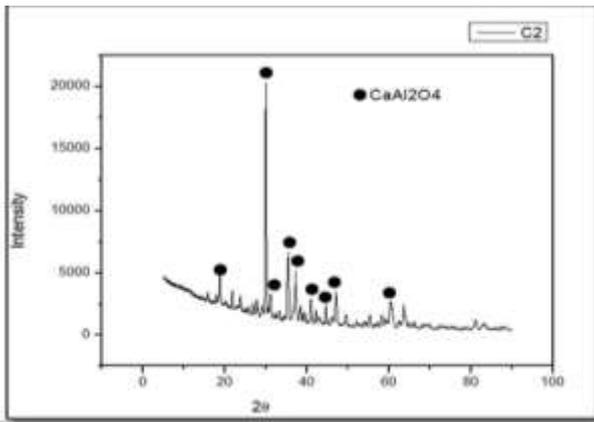


Fig. 10: XRD pattern of powders at the stoichiometric ratio 1 by solution Combustion synthesis

B. Scanning Electron Microscope Observations

Figure 11 and 12 show the SEM images of CaAl_2O_4 of porous morphology with plate like agglomerates ranging from 10 to 100 nm. The agglomerates are porous due to escaped number of moles of gases released in combustion reaction. Some particles are sintered to form big hard aggregates of 1-5 μm . Some isolated 100nm sized particles are also seen in CaAl_2O_4 powder. The formation of CaAl_2O_4 when used with urea as fuel shows that temperature given was enough to help the formation of the spinel powder. Associated gas evolution results in highly porous structure as the amount of gas increases agglomerates are more likely to break and form the porous structure as seen in the images.

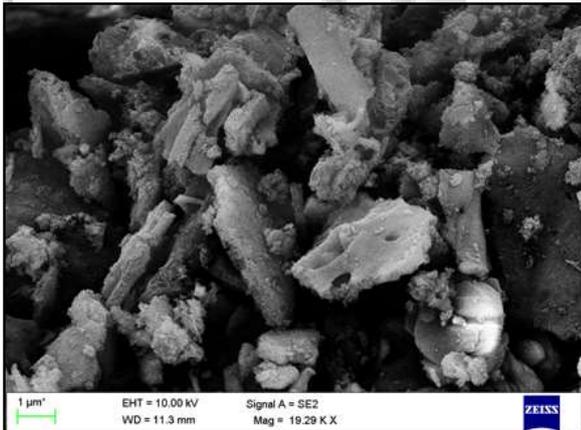


Fig. 11: SEM image showing Porosity developed due to escaped gases at fuel rich in variation of F/O ratio.

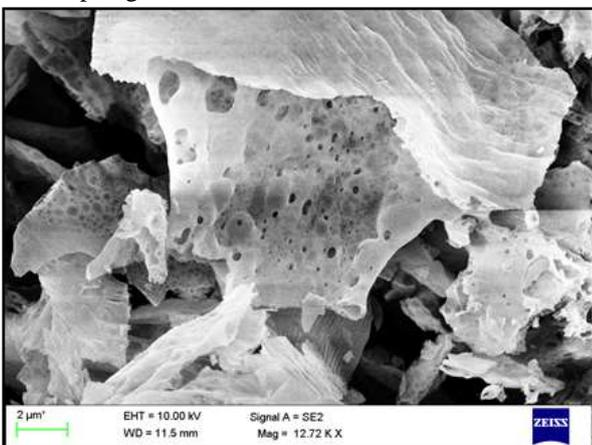


Fig. 12: SEM image showing agglomerates of CaAl_2O_4 powder.

IV. CONCLUSIONS

From the undertaken studies it was concluded that the amount of urea has a big influence on the morphological characteristic and phase composition of the product obtained by solution combustion synthesis. Although, the system comes to the equilibrium and pure calcium aluminate forms using stoichiometric amount of urea.

The end results are promising and the characterization results prove that the formation of Calcium Aluminate can be carried out at low temperatures (500 °C) using urea as fuel. More precisely it is a low cost and newer method of producing oxides.

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REFERENCES

- [1] M.A. Rodríguez *, C.L. Aguilar, M.A. Aghayan, "Solution combustion synthesis and sintering behavior of CaAl_2O_4 " Available online at www.sciencedirect.com, Ceramics International 38 (2012) 395–399.
- [2] Bhavya C., Yogendra K., Mahadevan K. M., "Synthesis of Calcium Aluminate Nanoparticle and Its Application to Photocatalytic Degradation of Coralene Navy Blue 3G and Coralene Violet 3R", Yogendra et al. Int. J. Res. Chem. Environ. Vol. 5 Issue 1 (28-33) January 2015.
- [3] J.M. Rivas Mercury¹, A.H. De Aza, P. Pena "Synthesis of CaAl_2O_4 from powders: Particle size effect", Journal of the European Ceramic Society 25 (2005) 3269–3279.
- [4] Amit Sharma, O. P. Modib and Gaurav K Guptab, "Effect of fuel to oxidizer ratio on synthesis of Alumina powder using Solution Combustion Technique- Aluminium Nitrate & Glycine combination", Advances in Applied Science Research, 2012, 3 (4):2151-2158.
- [5] K.S. Madhana Kumar a, L. John Berchmans, "Combustion synthesis of $\text{Ca}_{1-x}\text{Cu}_x\text{Al}_2\text{O}_4$ ($x = 0.0, 0.4$ and 0.8) copper doped calcium aluminate", Ceramics International 35 (2009) 1277–1280.
- [6] Leila Torkian¹, Mostafa M Amini², Zohreh Bahrami, "Synthesis of Nano Crystalline MgAl_2O_4 Spinel Powder by Microwave Assisted Combustion", Journal of Inorganic Materials Vol. 26 No. 5 May, 2011.
- [7] M. Shiran, M. J. Hadianfard, and M. M. Shiezadeh, "Synthesis of Nanocrystalline Electron Emissive Materials with Homogenous Composition in Nanoscale", International Journal of Chemical Engineering and Applications, Vol. 4, No. 3, June 2013.
- [8] Nguyen Ngoc Trac, "Photoluminescence Characteristics Of The CaAl_2O_4 : Eu^{2+} Co-Doped With Ion Dy^{3+} Synthesized By Combustion Method", International Journal of Chemistry and Materials Research, 2014, 2(8): 75-80.
- [9] Singanahally T. Aruna a,*, Alexander S. Mukasyan, "Combustion synthesis and nanomaterials", Current

Opinion in Solid State and Materials Science 12 (2008)
44–50, 2008 Elsevier Ltd. All rights reserved.

- [10] Milena Marroccoli, Maria Lucia Pace, “Synthesis of Calcium Sulfoaluminate Cements From Al₂O₃-Rich By-products from Aluminium Manufacture”, he University of Wisconsin Milwaukee Centre for By-products Utilization, Second International Conference on Sustainable Construction Materials and Technologies June 28 - June 30, 2010.

