Processing of Alumina Honeycomb Catalyst Substrates and Studies on Methyl Cellulose Binder Burn Out Kinetics

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Abstract: Alumina based honeycomb catalyst substrates are extrusion processed with methyl cellulose as a binder. Binder being organic in nature it reduces inter-particle friction thereby improves the flow ability while shaping and further enhances the mechanical strength of the green bodies. However, these binders are removed while further heat treatments through engineered heating schedules and any improper and non-uniform removal of these additives becomes a potential source of defects while processing cycles. In the present study, weight loss of the green honeycomb specimens was recorded as a function of temperature through Theromogarvimetric - Differential Scanning Calorimetric (TG-DSC) measurements at varying heating rates. A low heating rate less than 10°C/min up to 550°C is found to be desirable for binder removal. TG -Weight loss (x) with respect to the temperature can be regarded as $x = (M_o - M_T)/ (M_0 - M_f)$, where, M_o: initial weight, M_T: sample weight at temperature T and M_f: the final weight. Arrhenius parameters, for the thermal decomposition of the samples were determined by assuming a first order chemical reaction using the integral form of the rate law $dx/dt = Ae^{(-E/RT)} f(x)$. The plot of dx/dt vs 1/T exhibited a straight line and the activation energy for the burnout of methyl cellulose is estimated to be around 110 kJ/mole. The honeycomb samples were also subjected to sintering and the samples exhibited a highly porous microstructure and a compressive strength of 80 Kg/cm^2 suitable for catalyst coating.

Keywords: Catalyst Supports, Organic binder, Ceramic processing, Activation energy.

1. INTRODUCTION

Honeycomb structures are composites with one phase made up of inter connected network of solid struts with the other phase an empty space. Unlike solids, the properties of honeycombs are based on three major variables *i.e.* a) relative density (ρ^*/ρ_s where ρ^* is the density of the cellular material and ρ_s that of the solid of which it is made) b) cell wall material (polymer, metal, ceramics, glass, composites etc.) and c) geometry of the cells (cell size, equiaxed or anisotropic etc.). Today honeycomb structures with engineered configurations and thermo-mechanical properties are a novel class of advanced ceramics catering to diverse applications especially in energy and environment sector. Current and potential applications [1-5] of ceramic honeycombs ranges from high surface area supports for heterogeneous catalysis especially for environmental pollution control, biotechnology and biomedical applications, gas particulate filtration and fuel cell etc. These ceramic honeycombs are generally processed through extrusion processing, which generally starts with powders of optimum chemistry and physico-chemical properties. These powders should essentially have the free flow properties under shear to form the desirable engineering shapes. The flow ability while processing is generally achieved through the additives such as binders, plasticizers and lubricants [6-9]. Generally, these additives are organic in nature which in turn interact with the wetting medium and uniformly coat on the surface reducing the inter-particle friction and improving the flow ability. This will further enhance the mechanical strength of the green body by bonding the particle together. However, these binders are essentially burned out before sintering through a programmed heating schedule. When the binder is removed the strength of the green compact will decrease with a simultaneous pressure build-up from gaseous products resulting from thermal degradation of the binders [10]. If these binders are not removed under controlled conditions the raise of gas pressure that exceeds the stress tolerance of the components and the results in the introduction of defects such as air holes and cracks which are the potential source of rejection after sintering. This not only results in losses but also non biodegradable solid waste in the environment [11].

Methylcellulose is a well known binder used for the processing of ceramics and is composed of two components such as cellulose and methyl ($-CH_3$) side chains [12-15]. Cellulose itself is water insoluble, long chain molecule consisting of repeating anhydroglucose units. Cellulose with methyl substitution has very good compatibility characteristics with most of the common ceramic systems. In the present study alumina (α-Al_2O_3) a commonly used ceramic is extruded into

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catalyst substrates with honeycomb structure using 3.5w% of methylcellulose (concentration selected based on green strength optimization) as the binder and the binder burnout kinetics are studied using thermo gravimetric (TG) analysis. The honeycomb samples are further sintered to form the catalyst substrates with required cellular and thermo-mechanical properties.

2. EXPERIMENTAL PROCEDURE

Alumina (α- Al_2O_3) (MR01, Hindalco, India) samples were characterized for their physico-chemical properties such as chemistry, particle morphology and size as well as phase purity. Powder morphology and composition was assessed with scanning electron microscopy (SEM) and energy dispersive analysis (EDS) (Hitachi, Tokyo, Japan). Particle size was determined using photon correlation spectroscopy (DLS) (Nanosizer, Malvern, UK). Phase analyses were done by X-ray diffraction (XRD) using D8 advanced system and the XRD compared with the observed d-spacing and relative intensities with those of a reference material pattern compiled in the ICDD database. Crystallite size of the powder has been calculated using X-ray line broadening using the Scherrer equation , where crystallite size D = (0.9λ/βcosθ), λ, the wavelength of the radiation, β the corrected peak width at half maximum intensity, and 2θ the peak position. The samples were extruded into honeycomb structures using the techniques of Bagley and Lewis [16]. Alumina powder was mixed with 1 - 4 wt% of methyl cellulose as a binder and the mixture was further kneaded into an extrudable dough using water and poly-ethylene glycol as plasticizer. The samples were extruded into 45 x 4 x 3 mm specimens and estimated for green strength using the three point bend test (ASTM Standard C-1421). Based on the optimum green strength obtained for 3.5 wt% of methyl cellulose, dough prepared and was extruded using an in-house fabricated dies into honeycomb structures with square section having dimensions of 50 x 25 x 25 mm and were microwave dried. The green samples were characterized by thermo-gravimetric analysis using TG/DSC Simultaneous Thermal Analyser (STA449, Jupiter, Netzsch, Germany) and the weight loss was recorded as a function of temperature in static air up to 800°C. TGA experiments were carried out at the heating rates of 5°C/min, 10°C/min and 20°C/min. The corresponding weight loss (x) can be regarded as the reaction in progress with temperature and can hence

$$x = (M_o - M_T)/(M_0 - M_f) \tag{1}$$

(Where, M_o initial weight, $M_{T,}$ sample weight at temperature T, M_f final weight)

Arrhenius parameters, for the thermal decomposition of the samples were determined assuming a first order chemical reaction [17-21]. This method uses the integral form of rate law. The rate law of any solid phase reaction can be given as

$$\frac{dx}{dt} = A\, e^{(-E/RT)} f(x) \tag{2}$$

In non-isothermal TGA experiments the heating rate is varied as a function of time

$$\frac{dx}{dT} = \frac{dx}{dt} * \frac{dt}{dT} \tag{3}$$

$$\frac{dx}{dT} = \frac{dx}{dt} * \frac{1}{Y} \tag{4}$$

Where Y is the heating rate given by dT/dt

$$\frac{dx}{dT} = (A/Y)\, e^{(-E/RT)} f(x) \tag{5}$$

Plotting the left hand side against the 1/T gives E/R as the slope and A as the intercept. The honeycomb specimens are subjected to dilatometry up to 1600°C to record the sintering behavior and the green honeycomb samples further sintered to achieve required thermo-mechanical properties. Fracture surface of the honeycomb samples before and after sintering were also examined under scanning electron microscopy. The sintered samples were cut into cube of 10 x10x10 mm and compression strength was determined using a Universal Testing Machine.

3. RESULTS AND DISCUSSIONS

3.1. Powder Characterization

XRD pattern shown in Figure **1** corresponds to the phase pure α- Al_2O_3. Crystallite size of alumina estimated using the Scherrer equation is found to be 35 nm. The powder used in this study also has shown irregular morphology as is evident from SEM micrographs depicted in Figure **2**. Further, SEM pictures exhibited a particle size in the range of 0.6 - 1.0 microns complementing with the average particle size of 0.8 μm shown by by DLS technique. EDS analysis of the samples also exhibited a composition corresponding to Al_2O_3 stoichiometry without any major impurity

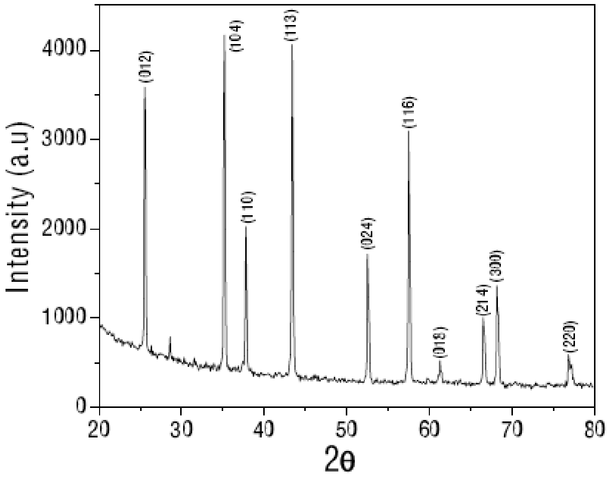

Figure 1: XRD pattern of Alumina powder.

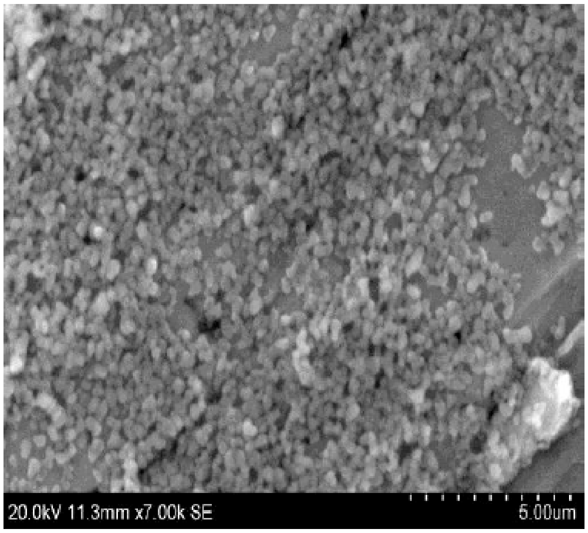

Figure 2: Morphology (SEM) of Alumina powder.

Figure **3** shows a plot of the flexural strength vs. the binder content for extruded rectangular bars. It clearly indicates that the mechanical strength of the samples increases as the percentage of binder content increase from 1 wt% to 3.5 wt% followed by no variation in flexural strength beyond this value. The minimum binder content which exhibits the maximum flexural strength is considered to be optimum as increase in binder content results in issues related to binder removal. Based on the flexural strength values binder content is considered to be optimum.

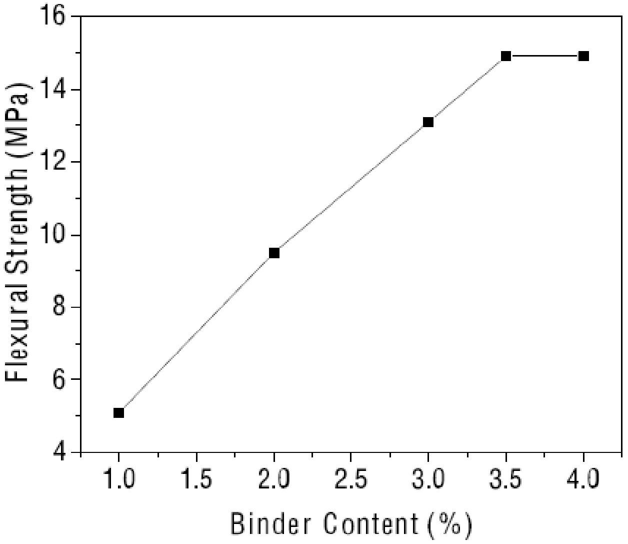

Figure 3: Flexural strength vs. binder strength for extruded specimens.

Typical honeycomb structure produced by extrusion processing is shown in Figure **4.a.** The samples are found to have 36 Channels Per Square Inch and a web thickness of 1.1mm. The extruded honeycombs have exhibited a relative density of 0.58 with the high geometrical surface area of 0.3514 cm^2/cm^3. Samples

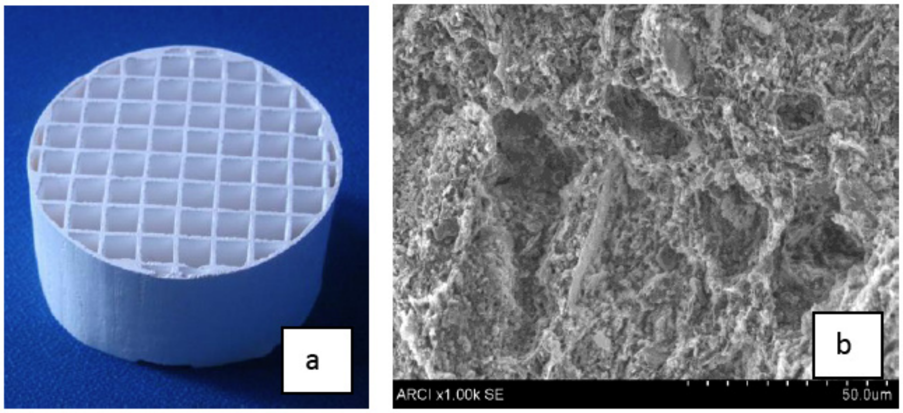

Figure 4: a. Green Honeycomb Samples Extruded and Dried and **b.** SEM images of Fracture surface of the extruded sample.

exhibited no visible defects in combination with good handilability. Fracture surface of the as extruded sample depicted in Figure **4b.** also indicates merging of the particles with the binder and a well packed microstructure.

3.2 Methyl Cellulose Burn Out Studies

Methyl cellulose burn out characteristic of extruded sample recorded using TG- DSC analysis is shown in Figure **5.** Binders in the green ceramics are generally removed by thermolysis in an oxidizing atmosphere. It is evident from the TG curve that when the samples exposed to a ramp rate of 5°C/min methyl cellulose start losing weight at around 180°C and continues to lose weight with relatively sharp transitions around 240 and 350°C. DSC shown in Figure **6**) plots also complements with strong endothermic and a weak exothermic peak in these temperature regimes. Thermal decomposition of methyl cellulose is generally occurs through the pyrolysis reactions such as primary and secondary thermal degradation. Chemical species of primary thermal decomposition resulting from depolymerisation or fragmentation may not be volatile, might undergo condensation or polymerization to form the chaar.

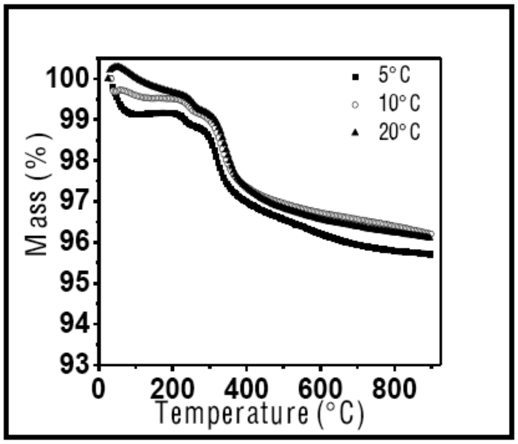

Figure 5: TGA (Weight loss vs. temperature) of Methyl Cellulose (5, and 10 and 20 °C/min).

Residual samples obtained after TG/DSC analysis with a high heating rate resulted in incomplete burning catalyzing the formation of the char. The blackening of the samples at a heating rate of 20°C/min confirms this observation. A heating rate of 10°C/min is regarded as optimum as the ash content in the sample is not observed. Further a close look at the residual samples also exhibited different types of defects such as cracks, bubbles etc. that are formed due to uncontrolled debinding. On faster heating there will be sudden release of gaseous products resulting from binder thermolysis which will raise the gas pressure causing the stresses within the pores of the matrix. Additionally, the strength of the green compact will decrease as the binder is removed with the simultaneous pressure build-up which exceeds the stress tolerance limits leading to cracks or blow holes. In order to avoid these defects, air holes and cracks it is important to select right organic additives and with optimum proportions.

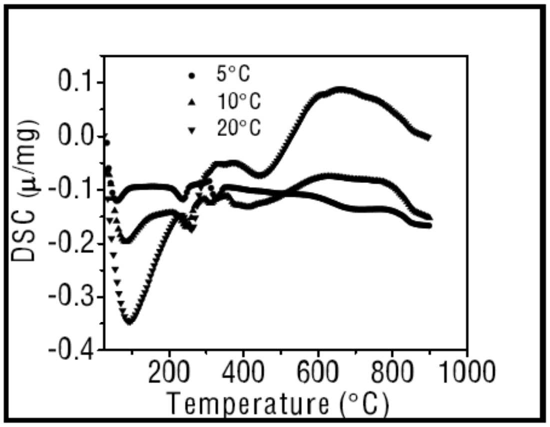

Figure 6: DSC (Weight loss vs. temperature) of Methyl Cellulose (3, 5, 10 and 20 °C/min).

3.3 Kinetics of Methyl Cellulose Pyrolysis

The data obtained from TGA studies are shown in Figure **7** for the heating rate of 5°C/min, 10°C/min and 20°C/min are used for the kinetic calculations. Extent of conversion ln [(dx/dT).Y.T] vs. 1/T is calculated as per the standard procedure depicted vide equations 1 to5 and the corresponding plot is shown in Figure **8.** The plot exhibits a straight line obtained by linear regression. The slope of the straight line gives E/R and the activation energy is estimated to be around 110 kJ/mole.

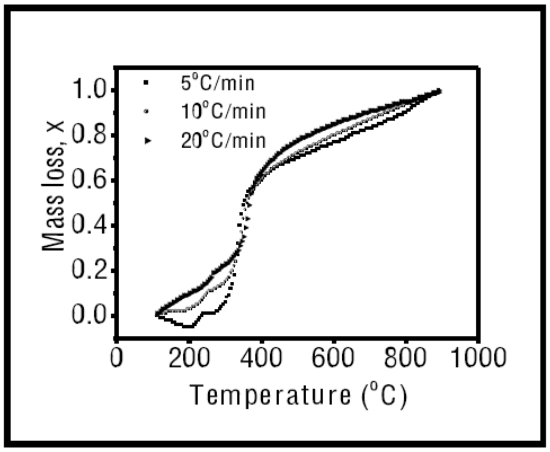

Figure 7: Mass loss vs. Temperature.

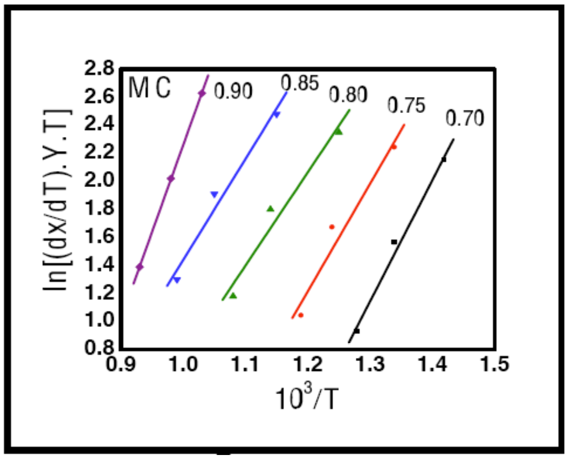

Figure 8: Plot of ln[(dx/dT).Y.T] versus 1/*T* gives the Arrhenius parameters *A* (pre-exponential factor) and *E* (activation energy) for MC.

3.4. Sintering of Extruded Honeycomb Sample

Dilatometric curve recoded for green honeycomb specimens are shown in Figure **9** indicating the sintering behavior. The sintered honeycomb and the fracture surface are shown in Figure **10.a** and **10.b** respectively. The honeycomb samples are found to have 49 Channels Per Square Inch and a web thickness of 0.9 mm. The extruded honeycombs have exhibited a relative density of 0.61 with the high geometrical surface area of 0.4178 cm^2/cm^3. It is evident from SEM fracture surface that the sintered samples are highly porous and further the samples exhibited a compressive strength of 80 Kg/cm^2. Honeycombs presently fabricated with the low thermal inertia, high geometrical surface area honeycombs in combination with highly porous microstructure and compressive strength of 80 Kg/cm^2 is expected to be the candidate substrate material for effective catalyst loading.

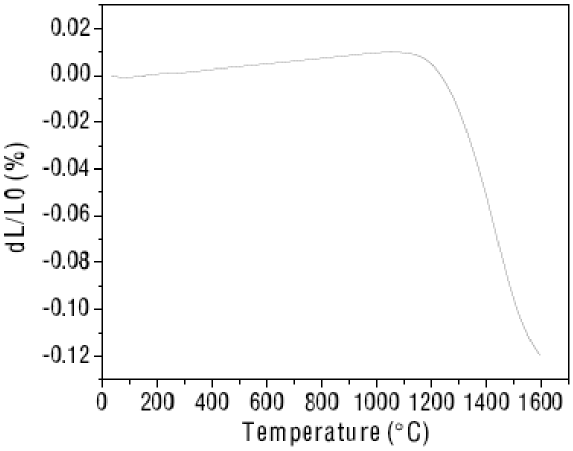

Figure 9: Dilatometer sintering plot.

CONCLUSIONS

Ceramic extrusion forming of honeycomb catalyst substrates were carried out with 3.5% of methyl cellulose as an organic binder. A binder content of 3.5 wt% is considered to be optimum as this concentration found to exhibit maximum flexural strength.

TG/DSC curves recorded have shown a feature to lose weight continuously with relatively sharp transitions around 240 and 350° C which also complemented with strong endothermic and a weak exothermic peak in these temperature regimes. Pyrolysis reaction of methyl cellulose occurs through primary thermal decomposition followed by the secondary thermal decomposition reactions. Blackening of residual samples with occasional defects obtained after TG/DSC analysis at 20°C indicates prominence of charring with high heating rates. Kinetic calculations based on the thermogravimetric data have shown activation energy of 110 kJ/mole for the thermal degradation of methyl cellulose.

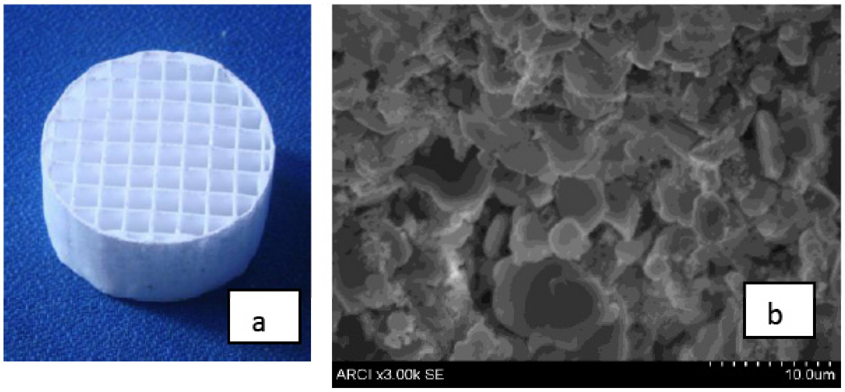

Figure 10: a. Sintered honeycomb and **b.** SEM fracture surface.

Sintered honeycombs have exhibited 49 Channels Per Square Inch and a web thickness of 0.9 mm with a relative density to 0.61 and a high geometrical surface area of 0.42 cm^2/cm^3. Further, honeycombs presently fabricated exhibits porous microstructure with an acceptable compressive strength of 80 Kg/cm^2 suitable for catalyst substrate applications.

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