

SYNTHESIS AND CHARACTERIZATION OF PRECURSOR FOR Al_2O_3 -MULLITE COMPOSITE DERIVED FROM DEHYDROXYLATED KAOLINITE

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ABSTRACT

With the objective of preparing a precursor powder for alumina-mullite composite through a non-conventional colloidal route and characterize the same, the present investigation was undertaken. The important physico-chemical characteristics like molar ratio, bulk density, surface area DTA, IR Spectrum of the synthesized mixed precursor powder were investigated. Equilibrium dehydration-rehydration characteristics of the hydrogel was also examined. The synthesized powders possessed significantly high surface area which followed a direct relationship with Al_2O_3 content in the composition. Thermal analysis of the precursor powder reflected the expulsion of both loosely bound gel water and dehydroxylation of aluminium hydroxide and the peak temperatures of DTA curves were influenced by the Al_2O_3 content. The nature of the Rehydration curves remained same irrespective of the mole ratio of SiO_2 : Al_2O_3 . The magnitude of rehydration was directly related to the Al_2O_3 content in the composition.

Keywords: Alumina, Mullite, DTA-TGA, Dehydration, Rehydration.

INTRODUCTION

Clays are most important among the widely distributed geological sediments and are the oldest ceramic materials. Beside the plastic property for which clay is indispensable the pyrochemical changes are of great significant in many industries which mostly include dehydration, phase transformation, solid reaction, sintering vitrification, etc [1-5].

Mullite is the ultimate stable crystalline phase in Al_2O_3 - SiO_2 system. Though clay is one of the most important naturally occurring sources for generation of mullite but according to the composition it cannot yields 100% mullite. Thus the ultimate microstructure contains mullite along with non-crystalline siliceous phases before fusion. The mullite phase has received significant attention as a potential matrix material for high temperature structural application [6-12]. With respect to reactivity and mixing co-precipitation and sol-gel methods are superior to conventional process of solid state mixing of naturally occurring materials. The objective of the present investigation was to convert the residual SiO_2 of dehydroxylated clay to mullite by reaction sintering process.

EXPERIMENTAL

Raw materials used in the present investigation were Rajmahal China clay, laboratory grade $\text{Al}(\text{NO}_3)_3$. The precursor powder formation occurred through a heterogeneous phase reaction in which the solid dehydroxylated clay was dispersed in 0.5 molar $\text{Al}(\text{NO}_3)_3$ solution and precipitation occurred both at the internal and external surfaces. The batch compositions were adjusted in such a manner that the molar ratio of $\text{SiO}_2:\text{Al}_2\text{O}_3$ were 1:1.5, 1:1.75 and 1:2 respectively.

Chemical analysis of the both the ingredient, clay and the precursor powder were carried out by following the classical Na_2CO_3 fusion method. Loose bulk density was determined by following the standard method. Specific surface area of clay and clay-alumina precursor powder was determined using surface area analyzer Model 1750 of M/s. Carlo Erba Strumentazione, Italy. IR spectra was taken by a Hitachi Spectrophotometer which was of dispershiv type. NETZSCH simultaneous thermal analyser STA 409 instrument was used for differential thermal analysis. The identification of different crystalline phase of the powdered clay was carried out by powder X-ray diffraction study. They were analyse in X-ray diffractometer of model D500 of Simens make with screening speed of $2^\circ(2\theta)$ per minute using Mo as target. The dehydration of the precursor powder was done at different temperature ranging from 100 to 800°C respectively and the rehydration study of the heat treated samples were performed at different humidity such as 35, 55, 75 and 100% relatively.

RESULT AND DISCUSSION

The physico-chemical characteristics of the experimental Rajmahal china clay are given in Table-I.

Table-I : Physico-chemical characteristics of Rajmahal china clay

Property	Percent present in purified kaolinite	
Chemical analysis	SiO_2	47.12
	Al_2O_3	39.11
	Fe_2O_3	0.68
	LOI	12.68
Molar ratio $\text{SiO}_2:\text{Al}_2\text{O}_3$	2.04	
CEC meq/100g	8.21	
Loose bulk density	0.54	
Surface area m^2/g	12.12	
DTA peak temperature $^\circ\text{C}$	573 (endothermic)	
	980 (exothermic)	

The chemical analysis indicated pure kaolinite nature of the experiential clay sample. This was confirmed by DTA curve (fig. 1) on exhibiting the strong endothermic peak at 573°C due to dehydroxylation of clay and sharp exothermic peak at 980°C associated with the crystallization of $\gamma\text{-Al}_2\text{O}_3$ or Al/Si spinel. The TG curve indicated the weight loss pattern having the same peak temperature. As that observe in the DTA themogram.

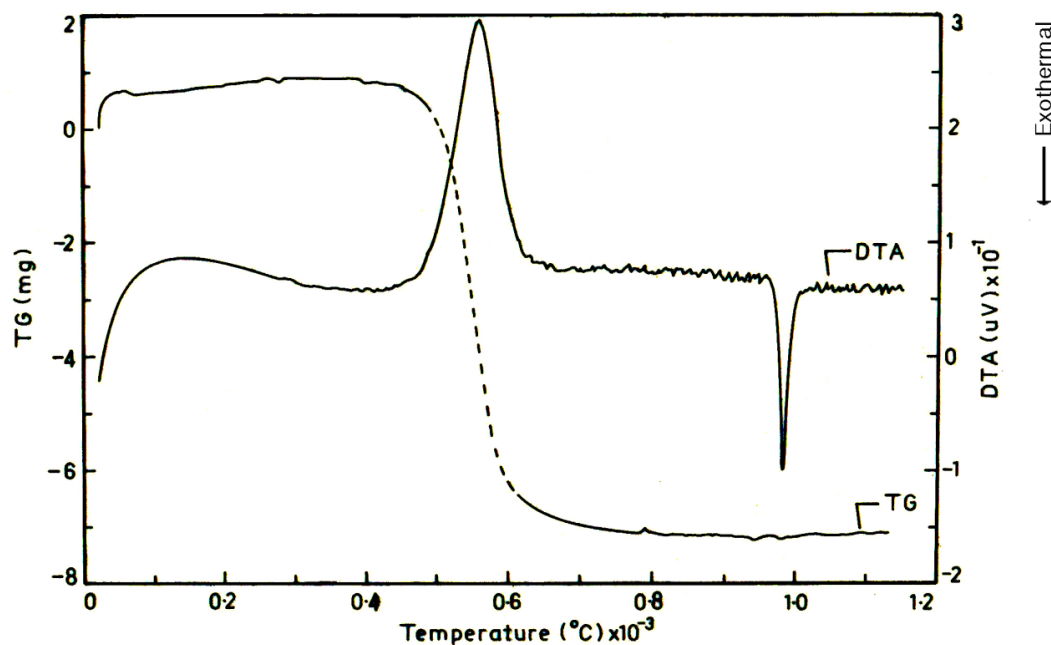


Fig.1: DTA characteristic of Rajmahal china clay

The X-ray diffraction pattern (fig.2) clearly indicated the presence of kaolinite as the major mineral phase along with trace of quartz.

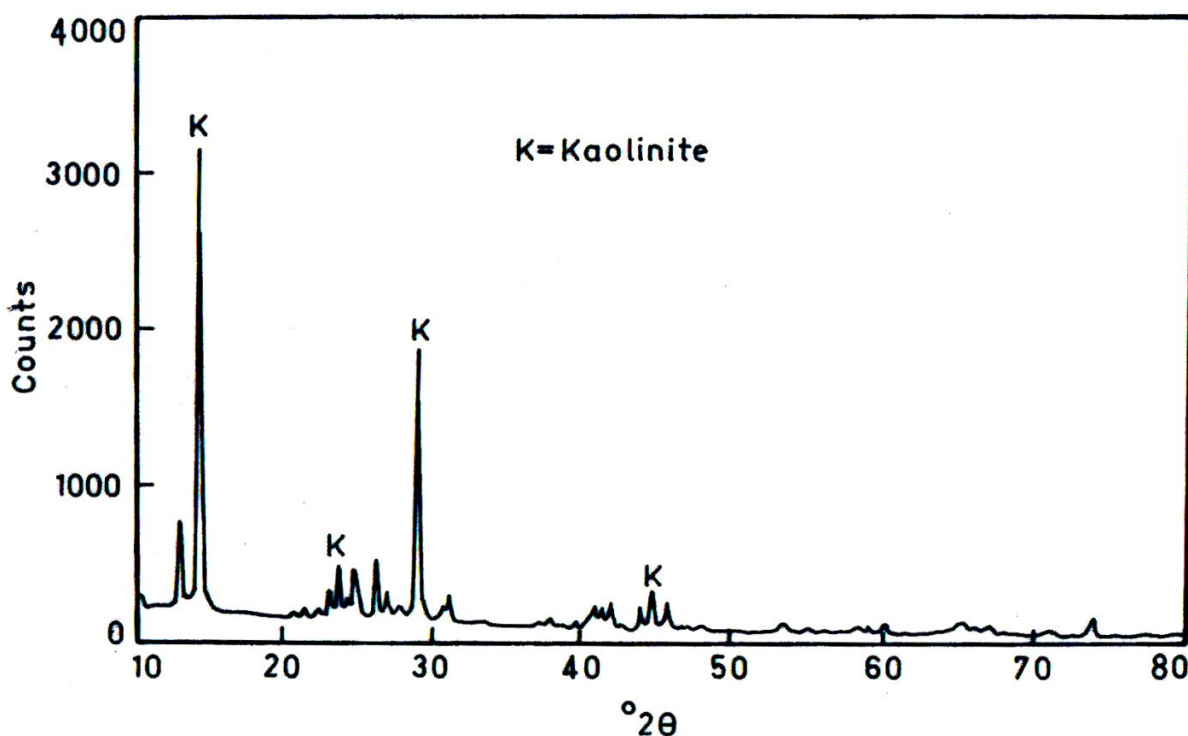


Fig.2: X-ray diffraction pattern of purified Rajmahal china clay

The important physic-chemical characteristics of the synthesized mixed precursor powder are given in Table-II.

Table-II: Physico-chemical characteristics of the synthetic hydrogel of Al_2O_3 - SiO_2 system

Property	$\text{SiO}_2:\text{Al}_2\text{O}_3$		
	1:1.5	1:1.75	1:2
Molar ratio $\text{SiO}_2:\text{Al}_2\text{O}_3$ (chemical analysis)	1:1.48	1:1.70	1:1.98
Bulk density (g/cc) of the loose powder	0.675	0.662	0.641
Surface area m^2/g	112	142	227
Physical texture	Opaque whitish granular semihard	Opaque whitish granular soft	Opaque whitish granular powdery
DTA peak temperature $^{\circ}\text{C}$	120, 285	115, 290	110, 295
	(endothermic)	(endothermic)	(endothermic)
	980	980	980
	(exothermic)	(exothermic)	(exothermic)

The hydroxides in the clay surfaces remained more or less in a state of mechanical mixture with no possibility of compound formation in aqueous phase. Aluminium hydroxide hydrogel contains hydroxo bridges and the fine particulate has different polymorphs depending on the nature of the hydroxide linkages. Regarding the growth of the gel around the dhydroxylated clay particles there was always some distortion in the orientation of the both primary and secondary ligands.

The bulk density of the loose powder was found to be an inverse function of Al_2O_3 in the composition. Sufficient lower bulk density of the powder indicated the fine texture with minimum agglomeration.

Infra red analysis (fig.3-5) of the hydrogel indicated the existence of all the related bond frequencies including OH-stretching and bending and the characterization of Si-O and Al-O vibration.

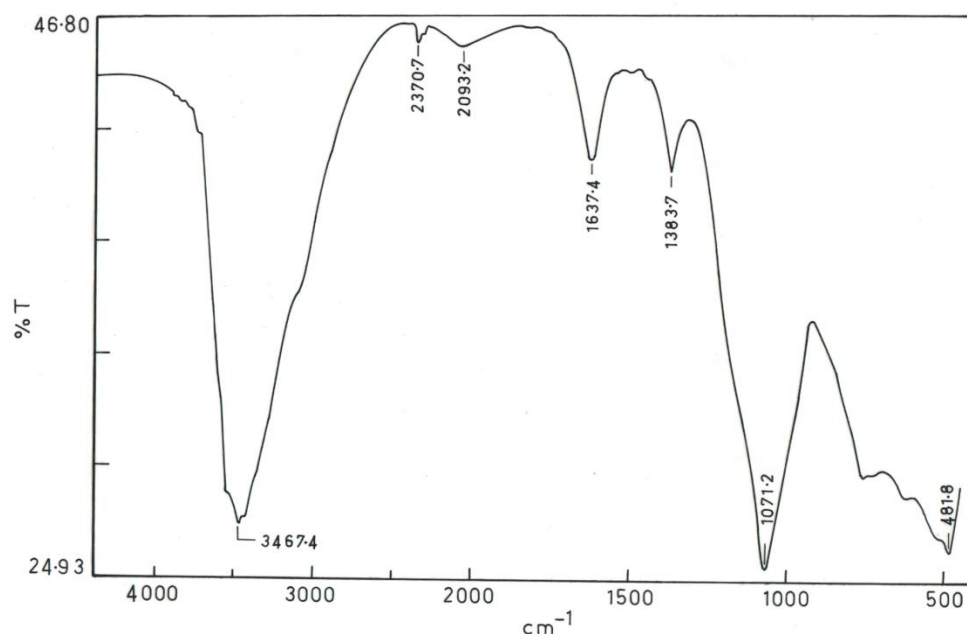


Fig.3: Infra-red spectrum of precursor powder having $\text{SiO}_2:\text{Al}_2\text{O}_3$ mole ratio 1:1.5

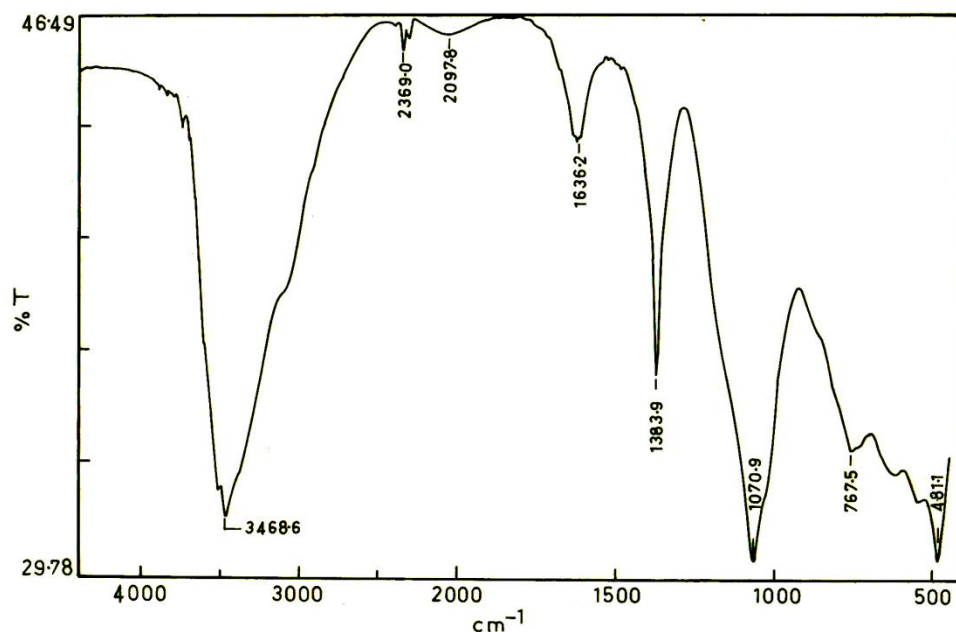


Fig.4: Infr-red spectrum of precursor powder having $\text{SiO}_2:\text{Al}_2\text{O}_3$ mole ratio 1:1.75

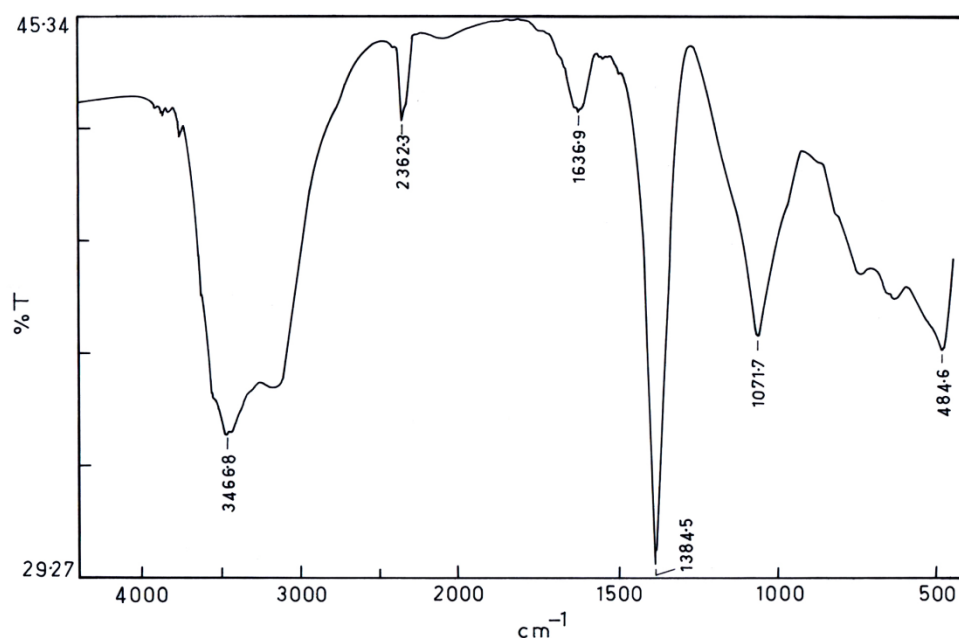


Fig.5: Infr-red spectrum of precursor powder having $\text{SiO}_2:\text{Al}_2\text{O}_3$ mole ratio 1:2

The differential thermal analysis of the precursor powders having different $\text{SiO}_2:\text{Al}_2\text{O}_3$ mole ratio was performed at a heating rate of $10^\circ\text{C}/\text{minute}$ and the thermograms have been represented in fig.6-8. The first endothermic peak at 110 to 120°C in the DTA diagram was due

to the expulsion of physically adsorbed gel water. The peak temperature followed an inverse relationship with Al_2O_3 content in the composition.

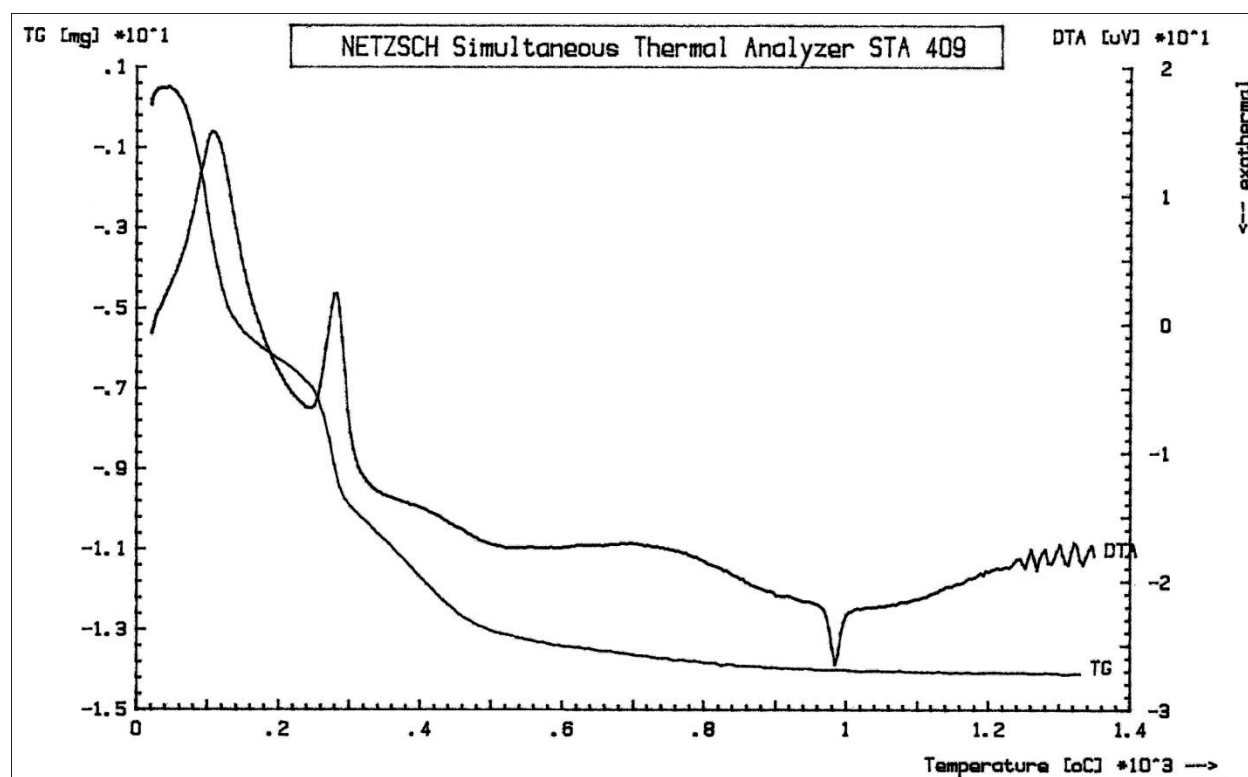


Fig. 6: DTA & TG characteristics of the Precursor powder having $\text{SiO}_2:\text{Al}_2\text{O}_3$ ratio 1:1.5

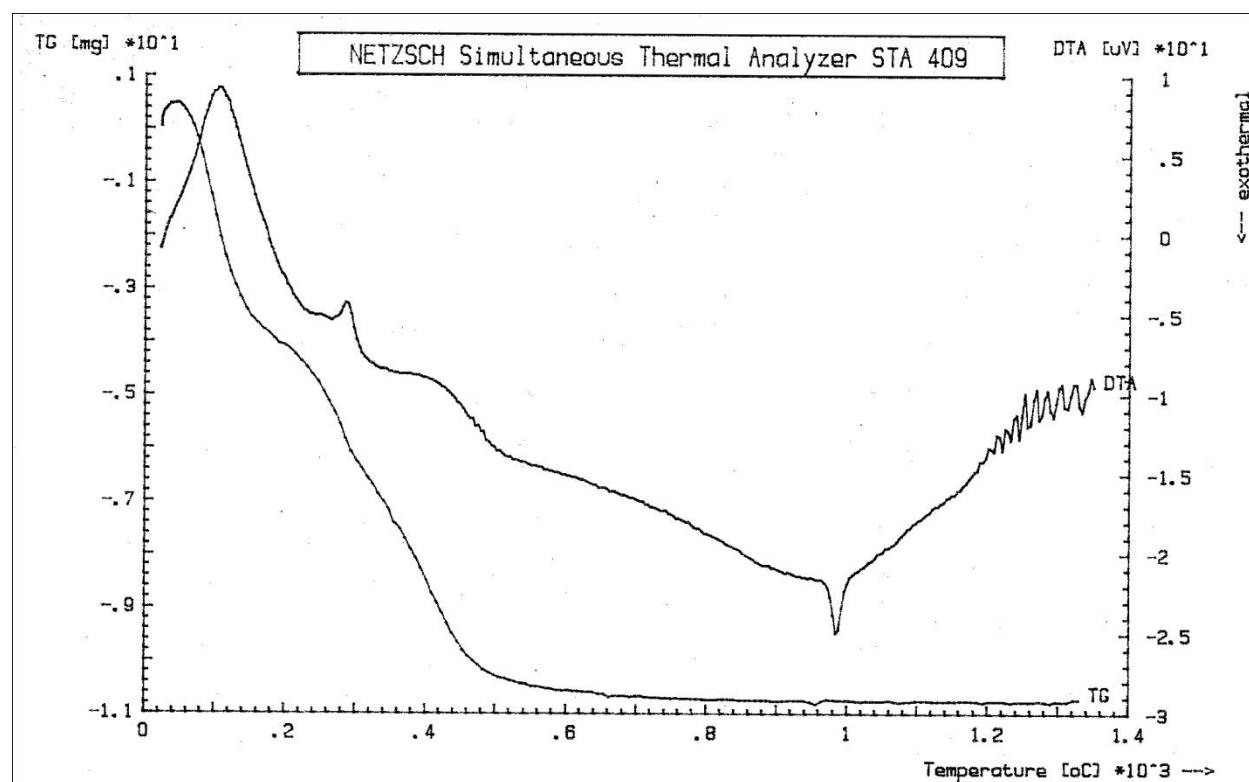


Fig. 7: DTA & TG characteristics of the Precursor powder having SiO₂:Al₂O₃ ratio 1:1.75

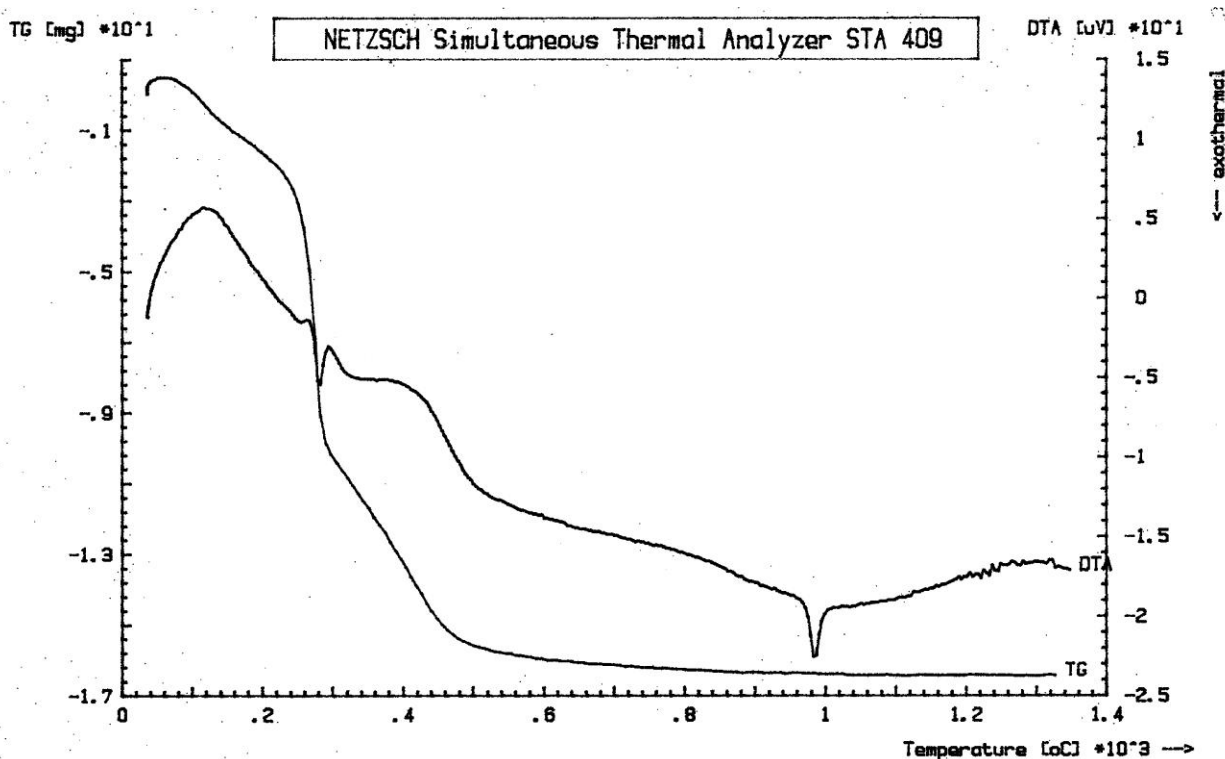


Fig. 8: DTA & TG characteristics of the Precursor powder having $\text{SiO}_2:\text{Al}_2\text{O}_3$ ratio 1:2

The second endothermic peak at 285-295°C was associated with the dehydroxylation of aluminium hydroxide. Though the variation of peak temperature was not of high order but it followed a direct relationship with Al_2O_3 content. The sharp exothermic peak at 980°C was due to crystallization of $\gamma\text{-Al}_2\text{O}_3$ from dehydroxylated clay or $\text{Al}_2\text{O}_3/\text{SiO}_2$ spinel formation. This reaction might be contributed by aluminium hydroxide also.

Difference in peak temperature in the DTA curve has led to the study of equilibrium dehydration-rehydration on progressive heat treatment. The nature of the dehydration curves (fig.9) was almost identical, irrespective of the molar composition.

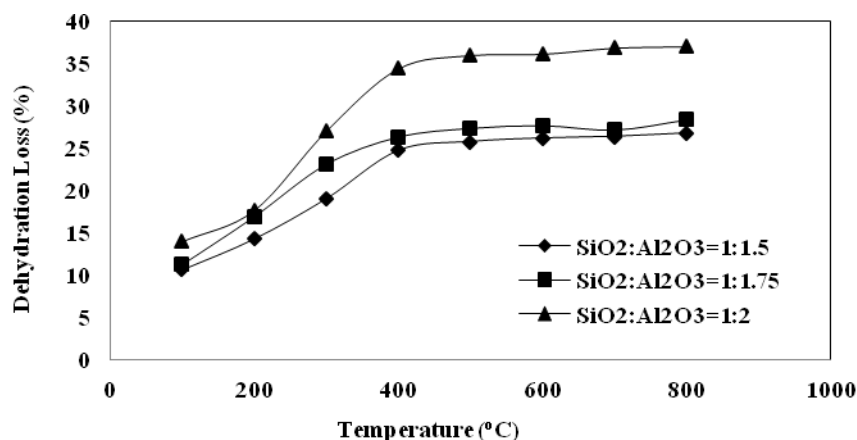


Fig. 9: Dehydration loss of the sample of various composition at different temperature

The equilibrium dehydration process did not exhibit a continuous relationship i.e., up to 400°C the dehydration rate was rather faster following which it slowed down. The inflection points remained unaltered indicating that the mechanism of expulsion was same. In the first stage up to 400°C the dehydration proceeded in a more or less linear path. When expulsion of water started the temperature of the surface of the gel dropped because of loss of heat due to the latent heat of vaporization of the liquid. However heat flow to the surface from the atmosphere quickly establishes thermal equilibrium, where transfer of heat to the surface balances the heat loss due to the latent heat of vaporisation with the increase of temperature became stiffer because new bonds were formed by condensation reaction and the porosity decrease.

In the second part of heat treatment curve the rate significantly decreased and here the liquid in the pores near the surface existed through channels that were continuous. This provided pathway for the liquid to flow to the surface. As the distance between the liquid vapour interface and the surface increased, the pressure gradient decreased and the flux of the liquid also decreased. Thus the thickness of the coating of aluminium hydroxide layer has positive influence on the rate curves.

In order to study the structural flexibility the dehydrated sample at each temperature was subjected to rehydration successively at four different humidities. As the extent of rehydration depends upon the weight of water lost during heat treatment the percentage rehydration was calculated from the following equation:

$$100 \times \frac{R}{D}$$

Where D = dehydrated weight and R = amount of rehydration on the basis of the dehydrated weight of the same sample after heat treatment.

It has been observed from the rehydration-temperature curve that:

- i) The nature of the rehydration curves (Fig. 10-13) remained same irrespective of the mole ratio of $\text{SiO}_2:\text{Al}_2\text{O}_3$. The sharpness of the peak decreased with increase of humidity indicating high surface hydration.

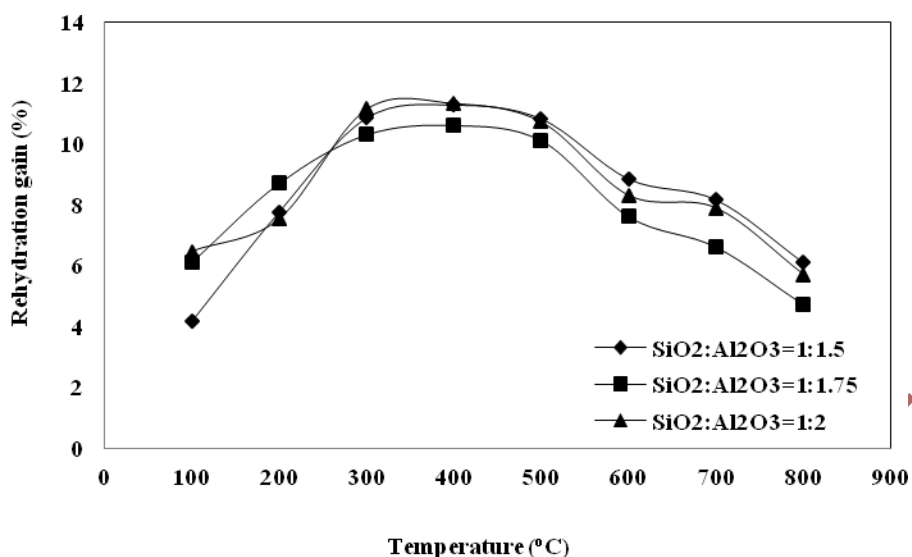


Fig. 10: Rehydration gain (%) of the hydroxide hydrogel in $\text{SiO}_2\text{-Al}_2\text{O}_3$ system at 35% relative humidity

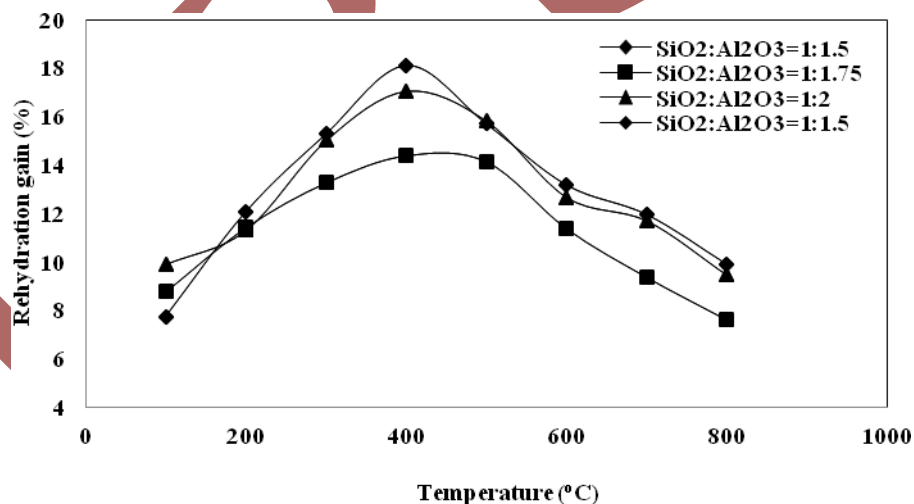


Fig. 11: Rehydration gain (%) of the hydroxide hydrogel in $\text{SiO}_2\text{-Al}_2\text{O}_3$ system at 55% relative humidity

- ii) The change of humidity did not influence the nature of the curves. The magnitude of rehydration initially increased up to 400°C for 35 and 55% and 500°C for 75 and 100% relative humidities and then decreased gradually up to the final temperature of heat treatment.

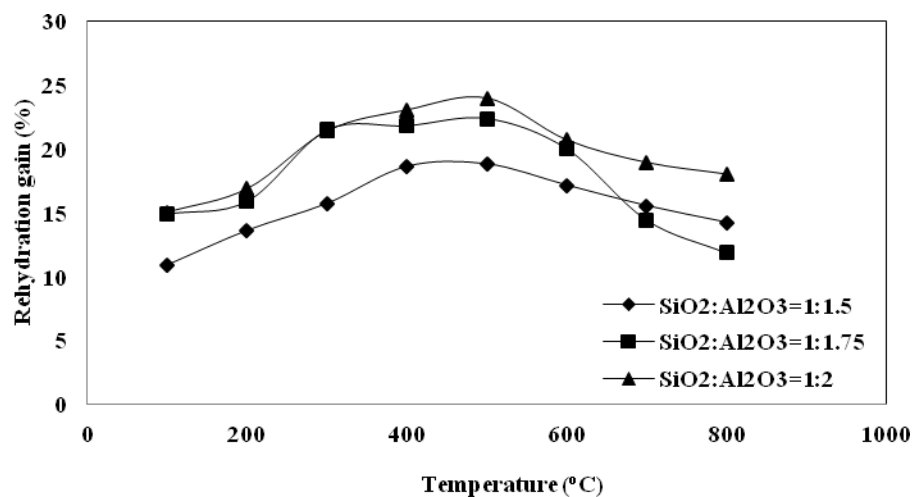


Fig. 12: Rehydration gain (%) of the hydroxide hydrogel in $\text{SiO}_2\text{-Al}_2\text{O}_3$ system at 75% relative humidity

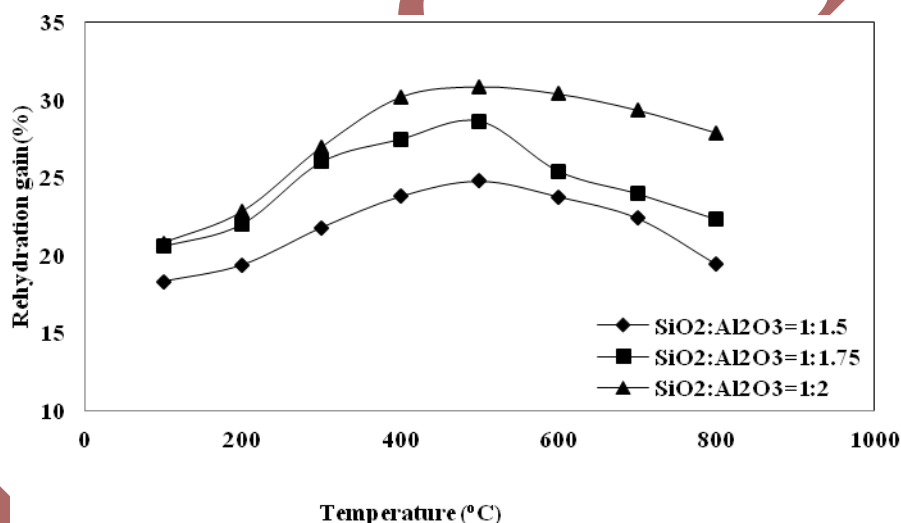


Fig. 13: Rehydration gain (%) of the hydroxide hydrogel in $\text{SiO}_2\text{-Al}_2\text{O}_3$ system at 100% relative humidity

iii) When the oxide surface gel dehydrated it tends to become hydrophobic. When cooled at room temperature rehydration was slow even though it was favored thermodynamically. Without surface OH group, water molecules back surface sites for forming hydrogen bonds and therefore physical adsorption of water was difficult. Since the formation of surface hydroxyl group was required as a preliminary step in the physical absorption of water, rehydration was retarded.

It appears from the above observations that the change of pore dimension occurred in an identical manner on heat treatment irrespective of compositional variation in the hydrogel. At

lower temperature the elimination of entrapped air might result in some expansion of pores. But with increase in temperature shrinkage occurred, causing a decrease in total rehydration capacity.

CONCLUSION

On the basis of the above results following may be concluded:

Chemical analysis of the dried product indicated that more or less same mole ratio of $\text{SiO}_2:\text{Al}_2\text{O}_3$ was retained as that in the batch compositions. High surface area followed a direct relationship with Al_2O_3 content in the composition. The thermal analysis of the precursor powder reflected the expulsion of both loosely bound gel water and dehydroxylation of aluminium hydroxide and the peak temperatures of DTA curves were influenced by the Al_2O_3 content. The hydroxide of aluminium was responsible for the dehydration-rehydration phenomenon as the clay has already been dehydroxylated before gelation. The dehydration loss at each temperature was directly related to Al_2O_3 content in the composition. Humidity effect has been manifested in two steps, rehydration was relatively fast up to 55% relative humidity beyond which the rate was slower.

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