

## Synthesis and characterization of $\text{ZnAl}_2\text{O}_4$ precursor in relation to different basic media

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The role of different basic media for the preparation of Zn-Al based hydroxy compounds, leading to the formation of  $\text{ZnAl}_2\text{O}_4$  spinel at low temperature was investigated. Nitrate salts of respective cations with molar ratio for ZnO :  $\text{Al}_2\text{O}_3$  as 1 : 1 were used for coprecipitation. DTA, TGA, XRD, IR spectroscopy and SEM technique were utilised for characterization of the precursor hydroxy compounds as well as the final products obtained by heat treatment of the hydroxy compounds at different temperatures. It had been found that spinel formation was very much influenced by the nature of mixed hydroxide precursors obtained by using different basic media. The thermal treatment of the coprecipitated gel powders led to the formation of  $\text{ZnAl}_2\text{O}_4$  at relatively low temperature (500°). Mixed hydroxide gel powder obtained by using  $\text{NH}_4\text{OH}$ -hexamethylene tetramine (HMT) as basic medium was observed to exhibit best results so far as spinel formation at low temperature was concerned.

Various attempts have been made to prepare  $\text{ZnAl}_2\text{O}_4$  spinel by solid state reaction using ZnO and  $\text{Al}_2\text{O}_3$  as starting materials and different parameters relating to kinetics, mechanism of the reaction and phase relations etc. were studied. In the search of high performance materials there is a challenge to synthesize binary oxides with improved properties relative to the individual oxide. In this context particle size reduction, homogeneity of the binary component, crystallographic nature and microstructure are the main controlling factors as far as the quality of final product is concerned.

Zinc and aluminium both are amphoteric in nature i.e. they form salts with acids and bases but their precipitation behaviour is somewhat different. Ammonia does not precipitate  $\text{Zn}^{2+}$  in presence of ammonium chloride which diminishes the concentration of  $\text{OH}^-$  ions of ammonium hydroxide to such an extent that the value of the ionic product  $[\text{Zn}^{2+}][\text{OH}^-]^2$  does not exceed the solubility product of  $\text{Zn}(\text{OH})_2$ , which therefore is not precipitated. Moreover addition of excess ammonia favours the formation of colourless complex hydroxide  $[\text{Zn}(\text{NH}_3)_4](\text{OH})_2$ <sup>1</sup>. But in case of  $\text{Al}^{3+}$ , the presence of ammonium chloride stabilizes the formation of  $\text{Al}(\text{OH})_3$  when  $\text{NH}_4\text{OH}$  is the precipitating agent.

Basic media play an important role in case of precipita-

tion reaction. It has been found that modification of the basic precipitating media and use of different solvent changes the grain size, shape of the particles in course of gelation process<sup>2,3</sup>.

While studying the kinetics and mechanism of the reaction between zinc oxide and aluminium oxide Branson<sup>4</sup> prepared  $\text{ZnAl}_2\text{O}_4$  by using fine grained high purity  $\text{Al}_2\text{O}_3$  and ZnO and concluded that the formation of ordered spinel occurred when the oxides mixture reacted at 800° and above. According to him deviation in the early reaction stages from the Valensi model is believed to be due to phase boundary controlled process. Tsuchida *et al.*<sup>5-7</sup> investigated the formation of  $\text{ZnAl}_2\text{O}_4$  using ZnO and different forms of  $\text{Al}_2\text{O}_3$ . They observed that reaction rate constant of  $\eta\text{-Al}_2\text{O}_3(\text{S})\text{-ZnO}$  system  $\rightarrow \text{ZnAl}_2\text{O}_4$  was found to be ninety times higher than that of  $\eta\text{-Al}_2\text{O}_3(\text{N})\text{-ZnO}$  system at 750°<sup>5</sup>, addition of small amount of chlorine or its compound  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  accelerated the reaction rate of  $\eta\text{-Al}_2\text{O}_3$  with ZnO<sup>6</sup> and reactivity of  $\theta\text{-Al}_2\text{O}_3$  was greater than that of  $\delta\text{-Al}_2\text{O}_3$  due to greater surface area<sup>7</sup>. Nakayama *et al.*<sup>8</sup> studied the effect of weak mixing method on the formation of  $\text{ZnAl}_2\text{O}_4$ . The authors used  $\text{Al}_2\text{O}_3$  (5.4  $\mu\text{m}$ ) and ZnO (0.3  $\mu\text{m}$ ) for the preparation of  $\text{ZnAl}_2\text{O}_4$ . They used Komatsu's model for the analysis of data and found that plots of Jander function versus the heating time gave straight lines. Finally the au-

thors concluded that two processing factors for the apparent low activation energies are due to the use of the active  $\text{Al}_2\text{O}_3$  which decomposed at low calcining temperature and that of the weak mixing temperature. Kawakami *et al.*<sup>9</sup> worked on the kinetics of formation process of  $\text{ZnAl}_2\text{O}_4$  and the effect of dispersion of reactants in reaction mixture. The authors used fine alumina and granulated zinc oxide for the preparation of  $\text{ZnAl}_2\text{O}_4$  and found that  $\text{ZnAl}_2\text{O}_4$  was formed in the agglomerated  $\text{Al}_2\text{O}_3$  around granulated  $\text{ZnO}$  and the product layers are formed according to diffusion law. Petrova *et al.*<sup>10</sup> investigated the phase relations in two binary systems viz.  $\text{MgAl}_2\text{O}_4$ - $\text{ZnAl}_2\text{O}_4$  and  $\text{MgAl}_2\text{O}_4$ - $\text{Mg}_2\text{TiO}_4$ . The authors obtained  $\text{ZnAl}_2\text{O}_4$  by solid state reaction using  $\text{Al}_2\text{O}_3$  and  $\text{ZnO}$  as starting materials. The authors observed that chemical analysis of the composition ( $\text{ZnO}/\text{Al}_2\text{O}_3$ ) from stoichiometry depended on the firing schedule. Finally they concluded that the solid solution formation in the  $\text{MgAl}_2\text{O}_4$ - $\text{ZnAl}_2\text{O}_4$  system proceeds by means of isovalent substitution of  $\text{Mg}^{2+}$  by  $\text{Zn}^{2+}$ . Adak *et al.*<sup>11-13</sup> developed a new technique for the preparation of different spinel powders using mixed metal nitrates and PVA solution. The authors reported that  $\text{ZnAl}_2\text{O}_4$  powder<sup>12</sup> heat treated at  $550^\circ$  showed uniform spherical size ranging between 20 and 30 nm.

The main objective of this paper is to develop a suitable route for the preparation of fine reactive  $\text{ZnAl}_2\text{O}_4$  powder at low temperature which finds wide applications as sintering aids for ceramic system and as electronic components.

## Results and discussion

DTA and TGA curves of the dried gel powders were shown in Figs. 1 and 2, respectively. All the gel powders contained hydroxyl group and on heating dehydration took place due to dehydroxylation. Z-1 gel powder contained zinc hydroxide [ $\text{Zn}(\text{OH})_2$ ] obtained by addition of calculated amount of  $\text{NH}_4\text{OH}$  solution to zinc nitrate solution.  $\text{Zn}(\text{OH})_2$  exists in different forms depending on the preparatory technique i.e. basic media used for preparation, temperature *etc.*<sup>14</sup>. DTA curve showed a sharp endothermic peak from 211 to  $245^\circ$  and a broad endothermic peak from 388 to  $509^\circ$  indicating that maximum dehydration occurred upto  $245^\circ$ . TG curve also showed a steep weight loss upto  $245^\circ$  and weight loss is almost constant around  $509^\circ$ . Similarly A-1 obtained by addition of  $\text{NH}_4\text{OH}$  solution to aluminium nitrate solution contained aluminium hydroxide [ $\text{Al}(\text{OH})_3$ ]<sup>15</sup>. Endo effects below  $110^\circ$  were due to adsorbed moisture in the gel matrix. Other endo-effects from  $120$  to  $243^\circ$ ,  $243$  to  $308^\circ$  and  $308$  to  $644^\circ$  were due to dehydration owing to the expulsion of water from hydroxyl groups.

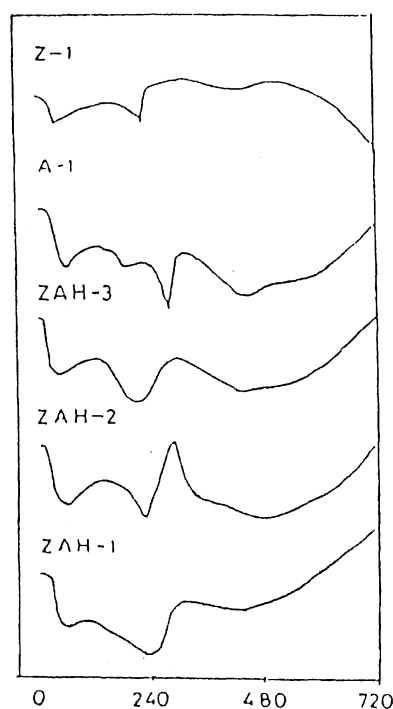


Fig. 1. DTA curves of the gel powders.

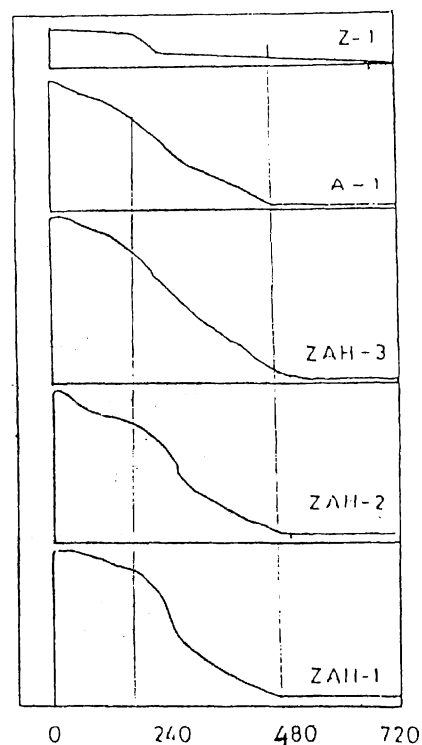


Fig. 2. TGA curves of the gel powders.

Corresponding weight losses were also noticed from the TG curve. Rest three systems (ZAH-1, ZAH-2 and ZAH-3) contained mixed hydroxides of zinc and aluminium obtained by the addition of three different basic medium viz.  $\text{NH}_4\text{OH}$ ,  $\text{NH}_4\text{OH-TEA}$  and  $\text{NH}_4\text{OH-HMT}$  respectively. In all cases endo effects below  $110^\circ$  were due to adsorbed moisture in the gel medium. In case of ZAH-1 sharp endothermic effect was observed upto  $300^\circ$  whereas broad endothermic effect was noticed upto  $500^\circ$  indicating the completion of dehydration. TG curve also showed that weight loss became minimum nearly at  $500^\circ$ . Similarly in case of ZAH-2 sharp endo effects were noticed upto  $280^\circ$  indicating that maximum dehydration occurred upto this temperature. An exothermic peak was observed at  $303^\circ$  which may be due to decomposition of triethanolamine (TEA) adsorbed in the gel matrix. In this case further dehydration was also noticed upto  $500^\circ$ . TG curve also showed maximum weight loss upto this temperature. In case of ZAH-3 sharp endo effect was observed upto  $290^\circ$  whereas broad endo effect was noticed upto  $500^\circ$ . Corresponding TG curve was similar to that of ZAH-2 showing weight loss almost constant at about  $500^\circ$ . So from the thermal analysis of mixed hydroxide system it may be concluded that dehydration caused by dehydroxylation was completed at around  $500^\circ$  in all cases and shift in peak temperature occurred due to difference in nature of the gel powders owing to the use of different basic medium for each of the system.

XRD patterns of the gel powder dried at  $110^\circ$  were shown

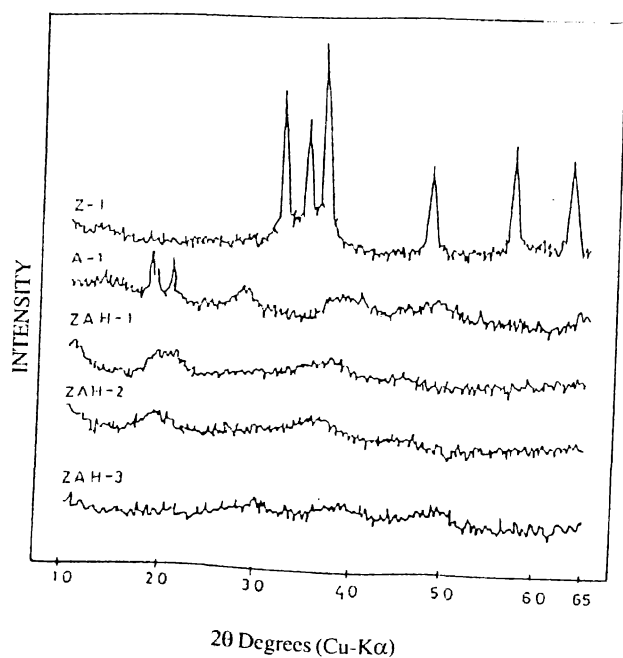


Fig. 3. XRD patterns of the gel powders dried at  $110^\circ$ .

in Fig. 3. Z-1 gel powder contained  $\text{Zn}(\text{OH})_2$  and showed well defined crystalline peaks of  $\text{Zn}(\text{OH})_2$ . A-1 gel powder obtained from  $\text{Al}^{3+}$  (nitrate) solution using dilute  $\text{NH}_4\text{OH}$  solution as basic medium showed very much poor crystallinity to X-ray diffraction. In all other cases of mixed hydroxide gel powder viz. ZAH-1, ZAH-2 and ZAH-3 obtained from the mix solution of  $\text{Zn}^{2+}$  and  $\text{Al}^{3+}$  (nitrate) using different basic media viz.  $\text{NH}_4\text{OH}$ ,  $\text{NH}_4\text{OH-TEA}$  and  $\text{NH}_4\text{OH-HMT}$  respectively showed amorphous nature. So it may be concluded that crystallinity of  $\text{Zn}(\text{OH})_2$  was hindered in case of mixed hydroxide coprecipitation and maximum amorphousity was observed in case of ZAH-3 where  $\text{NH}_4\text{OH-HMT}$  was used as basic medium.

All the mixed hydroxide gel powders (ZAH-1, ZAH-2 and ZAH-3) were subjected to heat treatment at  $500^\circ$  (referred as ZA-15, ZA-25 and ZA-35, respectively) and  $800^\circ$  (referred as ZA-18, ZA-28 and ZA-38, respectively) for 2 h and the patterns were shown in Figs. 4 and 5 respectively. In case of ZA-15, ZA-25 and ZA-35 crystalline peaks of  $\text{ZnAl}_2\text{O}_4$  were noticed and maximum crystallinity occurred in case of ZA-35 where  $\text{NH}_4\text{OH-HMT}$  was used as basic medium for mixed hydroxide gelation. As reported earlier by Adak *et al.*<sup>13</sup> it was found that utilising PVA technique no crystalline peak of  $\text{ZnAl}_2\text{O}_4$  was observed using mix metal nitrate as precursors heat treated at  $500^\circ$  for 2 h. It has been found that crystallinity increased with further increase in heat treatment temperature ( $800^\circ$  for 2 h) and maximum crystallinity was observed in case of ZA-38 when compared with ZA-28 and ZA-18 respectively.

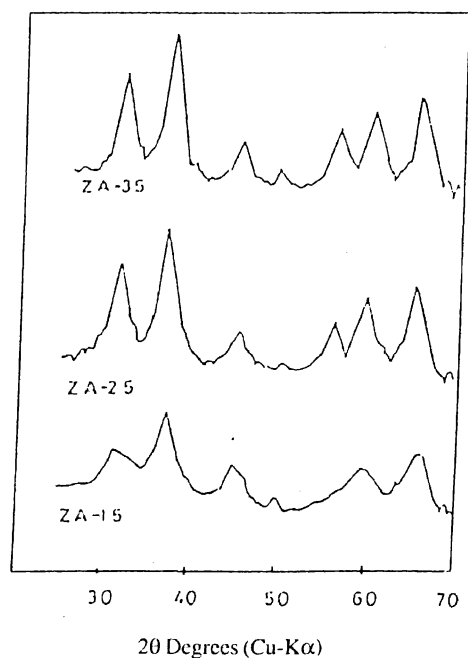


Fig. 4. XRD patterns of the coprecipitated gel powders heat treated at  $500^\circ$ .

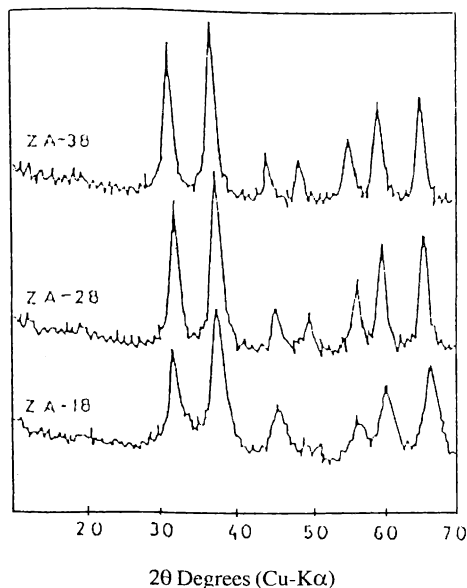


Fig. 5. XRD patterns of the coprecipitated gel powders heat treated at  $800^\circ$ .

IR spectra of the mixed hydroxide gel powders heat treated at  $800^\circ$  for 2h were shown in Fig. 6. In all cases bands around  $672$ ,  $564$  and  $508\text{ cm}^{-1}$  were found which corresponded to spinel structure<sup>13,16,17</sup>. Maximum intense peak was noticed in case of ZA-38 where  $NH_4OH$ -HMT

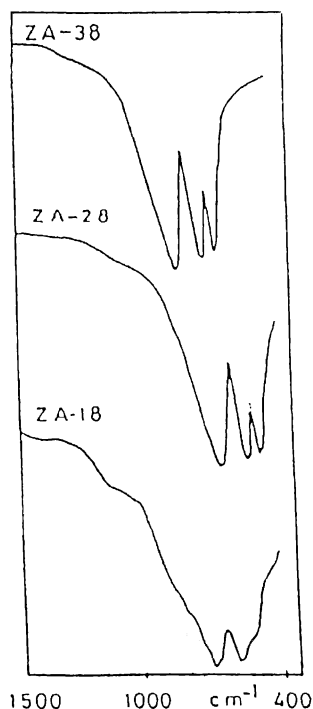


Fig. 6. IR spectra of the coprecipitated gel powders heat treated at  $800^\circ$ .

was used as basic medium for the preparation of mixed hydroxide. This fact was also supported by X-ray studies. Fig. 7 showed SEM micrograph of powdered sample (ZA-38) heat treated at  $800^\circ$  for 2 h. It was observed that the



Fig. 7. SEM micrograph of  $ZnAl_2O_4$  powder heat treated at  $800^\circ$  for 2 h.

particles were spherical shaped and the sizes ranged from  $0.12$  to  $0.21\ \mu\text{m}$ .

#### Conclusions :

Zn-Al based hydroxy compounds were prepared using different basic media for the synthesis of  $ZnAl_2O_4$  spinel at low temperature. Results were summarised as follows :

(1) Thermal analysis and XRD patterns showed that coprecipitated gel powders were not a mixture of individual hydroxide.

(2) Basic media played an important role during the preparation of precursor hydroxy compound used for obtaining  $ZnAl_2O_4$  spinel at low temperature.

(3) XRD patterns showed that spinel formation took place at  $500^\circ$  and the best result was noticed by the coprecipitate (ZAH-3) obtained by using  $NH_4OH$ -HMT as basic medium. Crystallinity of spinel increased with further increase of temperature.

(4) Spinel formation was further confirmed by IR spectroscopic analysis.

(5) Spinel powder ( $800^\circ$ ) showed spherical shape (ZA-38) ranging from  $0.12$  to  $0.21\ \mu\text{m}$ .

#### Experimental

##### Raw materials :

Analytical reagent grade nitrates of zinc and aluminium were used as starting materials. For the preparation of basic media, laboratory reagent grade ammonium hydroxide (25% solution sp. gr. 0.90), triethanolamine (TEA)  $[(CH_2OHCH_2)_3N]$  (97% solution sp. gr. 1.12), hexamethylene tetramine (HMT)  $[(CH_2)_6N_4]$  were used.

**Preparation of basic media :**

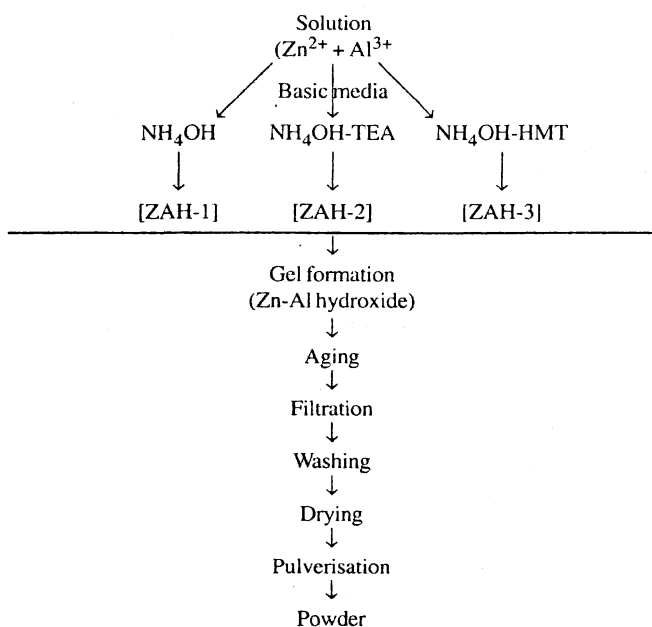
Three types of basic medium viz. (1) ammonium hydroxide diluted with water (1 : 20), (2) 0.01 mole (CH<sub>2</sub>OHCH<sub>2</sub>)<sub>3</sub>N (TEA) per 100 ml of ammonium hydroxide solution (1 : 20) and (3) 0.01 mole (CH<sub>2</sub>)<sub>6</sub>N<sub>4</sub> (HMT) per 100 ml of ammonium hydroxide solution (1 : 20) were used for the preparation of mixed hydroxide gel powders. Referred systems, precursor salt solution, corresponding basic medium and end product were shown in Table 1.

**Table 1.** Referred systems, precursors salt solutions, basic media and end product during the preparation of gel powders

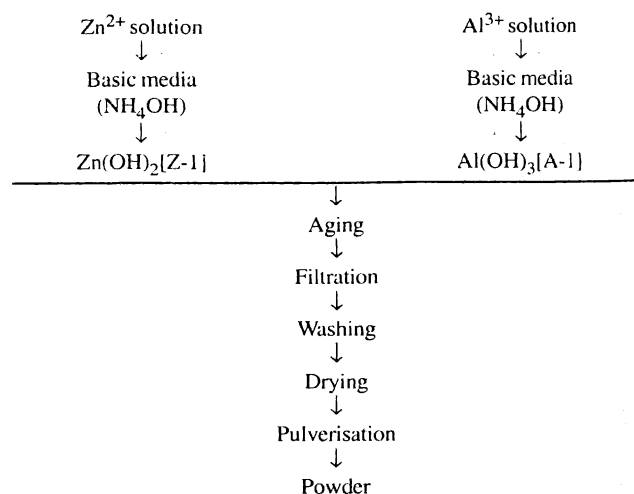
Referred system	Precursor salt solution	Basic medium	End product
Z-1	Zn <sup>2+</sup> (nitrate)	NH <sub>4</sub> OH	Zn(OH) <sub>2</sub>
A-1	Al <sup>3+</sup> (nitrate)	NH <sub>4</sub> OH	Al(OH) <sub>3</sub>
ZAH-1	Zn <sup>2+</sup> , Al <sup>3+</sup> (nitrate)	NH <sub>4</sub> OH	Zn-Al hydroxide
ZAH-2	Zn <sup>2+</sup> , Al <sup>3+</sup> (nitrate)	NH <sub>4</sub> OH-TEA	Zn-Al hydroxide
ZAH-3	Zn <sup>2+</sup> , Al <sup>3+</sup> (nitrate)	NH <sub>4</sub> OH-HMT	Zn-Al hydroxide

**Preparation of gel powders :**

Basic media (Table 1) were added dropwise into the mixed nitrate solution (0.1 M) with constant magnetic stirring. After completion of precipitation the gels were allowed to age for 24 h followed by filtration, washing with hot distilled water, drying at 110° and pulverisation. Following the same procedure individual hydroxide was also



**Scheme 1.** Schematic diagram for the preparation of mixed hydroxide gel powders.



**Scheme 2.** Schematic diagram for the preparation of individual hydroxide gel powders.

prepared using only ammonia solution as precipitating agent. A schematic diagram for preparing the gels with various basic media is shown in Schemes 1 and 2.

**Characterisation :**

Differential thermal analysis and thermogravimetric analysis were carried out to study the thermal behaviour of the gel powders by Shimadzu DT-30 and DT-50 Japan, respectively. The gel powders were subjected to heat treatment at different temperature and the identification of various phases was carried out by X-ray diffraction using Philips Diffractometer pw-1734 instrument, Ni filtered CuK<sub>α</sub> radiation was used for analysis at scanning rate 2° min<sup>-1</sup>. Mixed hydroxide gel powders calcined at 800° for 2 h were subjected to IR spectroscopic analysis using Perkin-Elmer FTIR-1615. Shape and size of heat treated powders were investigated utilising SEM technique using Leo-S4301, U.K.

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