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Synthesis, characterization and dehydration–rehydration study of sol-gel derived hydroxide hydrogel of the MgO–ZrO$_2$ system

A mixed hydroxide hydrogel of the MgO–ZrO$_2$ system has been synthesized by wet interaction in the aqueous phase. Both the mole ratio of MgO : ZrO$_2$ and the preparatory conditions strongly influence the particle morphology. This was also reflected in the dehydration–rehydration characteristics studied under equilibrium conditions. Both dehydration and rehydration followed a discontinuous path thereby indicating heterogeneity in the bonding of water to the gel structure.

Keywords: Zirconia; Magnesia; Sol-gel; Dehydration; Rehydration

1. Introduction

Colloidal consolidation routes provide the required control over the mechanism of particle–particle interaction. Generally agglomerated powder results in poor mixing and packing density variation in the consolidated compact. Many advances have occurred in the preparation of powders, forming and method of densification in recent times. Transformation processing includes manipulation of various types of sols, gels and organometallic precursor at low temperature, as well as change in the phase state of these substances at elevated temperature.

The performance of the composite is dependent on the physico-chemical relationship of the matrix, reinforcement and the interface. There are two approaches to producing ceramic matrix composite (CMC), one with a low volume percent of particle and the other with a high volume percent (40–50%). The characteristics of the precursor powder viz., particle size, shape, size distribution, degree of agglomeration etc., exert a profound influence on the densification and development of microstructure. The effect of preparation of a MgO–ZrO$_2$ composite via the sol-gel route on the sintering behaviour of the precursor powder is a subject of wide interest.

Li and Hon [1] prepared ultra-fine MgO–ZrO$_2$ powder which showed high sinterability, by freeze drying cubic ZrO$_2$ with 10 mol.% of MgO. Muccillo and Aliva [2] synthesized zirconia-based solid electrolyte powder using co-precipitation. The most significant feature of MgO–ZrO$_2$ is the decomposition of the cubic solid solution below 400 °C. As this occurs MgO has a tendency to precipitate at

the inter-granular voids. Eiji et al. [3] studied the corrosion behaviour MgO–ZrO$_2$, CaO–ZrO$_2$ sintered bodies where they have concluded the relevant mechanism. Water is an essential part of all types of synthetic hydrogels prepared in the aqueous phase through a colloidal route. The dehydration behaviour depends on the nature of bonding of water molecules. The bonding energy of the associated water is strongly influenced by the surface charge of the framework structure. The dispersion phase which is bonded with relatively low energy is normally expelled during drying. The residual water controls the physical texture of the material and is attached fairly strongly to the hydrophilic surface of the gels.

Fernandez and Franco [4] studied the low temperature dehydration of ZrO$_2$ gels and reported that a higher pH of precipitation and low temperature of dehydration are the best conditions to get the most micro-porous samples. At a lower pH the samples have a narrow pore size distribution together with a small pore size and pore volume. Mitra et al. [5] studied the equilibrium dehydration–rehydration behaviour of Ni, Co, Mn, Cu, Zn, Cd from synthetic zeolite in the temperature range of 70–600 °C. They observed that the equilibrium rehydration curve was always in conformity with the corresponding dehydration curve. The irreversibility of the heat treated hydrogel samples was due to the structural changes during heat treatment. Smdie and Radanyia [6] studied microstructure control in sol-gel derived alumina–zirconia composites. These were prepared via two sol-gel routes: one by mixing of the two sols and the other by peptizing Al$_2$O$_3$ by ZrO$_2$ salts. Transformation temperature to α-Al$_2$O$_3$, t-ZrO$_2$ and tetragonal to monoclinic ZrO$_2$ are somewhat higher in the second route and final grain size of ZrO$_2$ and Al$_2$O$_3$ are also larger. Experiments have been conducted to measure the temperature of the crystals during dehydration by Cooper and Garner [7] at a sufficiently low temperature where the rate of movement of the interface is slow and where cooling effects are negligible.

The sol-gel process [8–10] is used widely these days for preparing tailor-made synthetic precursor powder. Setu [11] prepared fine powders of MgO · ZrO$_2$ using inorganic metal salts by co-precipitation and also by sol-gel. After calcining at different temperatures the crystalline nature of the precursor was ascertained through X-ray diffraction (XRD). XRD of powder is a technique used to characterize the crystallographic structure, crystallite size (grain size)

and preferred orientation in solid samples. Thermal decomposition and phase transition were studied through thermogravimetric analysis (TGA) and differential thermal analysis (DTA). The DTA identifies the temperature regions and the magnitude of critical events during a drying or firing process while TGA measures the weight loss of a material in drying or in chemical reactions that liberate gases such as structural water release, structural decomposition etc. The TGA also measures the weight gain of a material from rehydration process.

2. Experimental procedure

2.1. Synthesis of the mixed hydroxide hydrogel

Wet interaction in the aqueous phase was followed for the synthesis of the hydrogel. Water soluble ingredients having minimum tendency to hydrolyze viz., $Mg(NO_3)_2$ and $ZrOCl_2$ were taken and dissolved in deionized water. Solution mixtures were prepared at three different mole ratios of $MgO:ZrO_2$ by taking requisite volumes of the individual solutions. In each case the solution concentration was adjusted to 5 % w/v. Then 1 : 1 ammonia solution was slowly added with continuous stirring until the whole mixture set into an enblocked gel at pH 9. The set gel was allowed to age for 24 h, whereby synersis occurred indicating perfect gel formation. The aged gel was dispersed in large bulk of water and allowed to settle. The supernatant clear liquid was carefully siphoned off followed by addition of fresh water. This process was repeated until the settled mass showed the tendency to disperse. Then it was filtered through a Buckner funnel, washed with hot deionised water and finally dried under vacuum at 50 °C.

2.2. Analysis

Chemical analysis was carried out to ascertain the molar ratios of $MgO:ZrO_2$ in the synthetic hydrogels. An accurately weighed and finely ground sample was dissolved in 1 : 4 H_2SO_4 solution. Zirconium hydroxide was precipitated from the solution by addition of NH_4OH-NH_4Cl buffer at pH 10.2. The solution was filtered, washed with deionized water and the residue was ignited to get ZrO_2 content. From the filtrate MgO was estimated complexometrically with EDTA in presence of solochrome black-T indicator.

NETZSCH Simultaneous Thermal Analyzer STA 409 was used for differential thermal analysis (DTA). The method is based on enthalpy change which occurs when a material undergo physical or chemical change on heating or cooling. About 0.2−0.3 g of accurately weighed sample was taken in a crucible and placed inside a closed tubular furnace. The temperature of the furnace was raised at the rate of $10 \, K \, min^{-1}$ to maximum temperature of 1 200 °C. α-Al_2O_3 was used as reference material. The temperature differences of the test sample with respect to reference sample during heating were recorded in DTA diagram. Surface area and particle size distribution of the precursor powders were measured using a Carle Erba Strumentazione of Italy (Model No. 1750 Sorpty) which is based on gas adsorption BET principle (using N_2 adsorption). Infrared analysis was carried out in Hitachi Spectrometer (270-90) in KBr phase. A small amount of accurately weighed sample was mixed thoroughly with KBr in an agate mortar and a disc was pre-

pared under vacuum at a pressure of $33 \, kg \, cm^{-2}$. The operational mode was double beam ratio recording type in which the absolute values of radiation intensity ratio in both reference and sample beam were continuously monitored.

X-ray diffraction analysis of all the samples was carried out in D5000 X-ray diffractometer (Siemens) with scanning speed of 2° (2θ)/min. The D5000 measures atomic spacing in crystals using diffraction of approximately monochromatic X-radiation. The radiation used is copper k-alpha with a wavelength of 1.5418 Å. The intensity of X-ray diffraction was plotted against angle of incidence. Scanning electron micrographs of all the samples were carried out in a Quanta 3D 200 (FEI) to study the particle morphology.

2.3. Equilibrium dehydration−rehydration study

Dehydration is an equilibrium heat treatment process whereby an accurately weighed sample is allowed to attain thermal equilibrium at a fixed temperature and the change in weight is recorded to calculate the weight loss. A definite quantity of the hydrogel (2 g in each case) was placed in a porcelain crucible and heated in an electrically heated muffle furnace at a selected temperature up to the point of equilibrium. The temperature of heat treatment was varied from 100 °C to 800 °C at 100 °C intervals. The equilibrium time was 2 h at each temperature.

After dehydration at a particular temperature, the heat treated samples were successively equilibrated at relative humidities of 35 %, 55 %, 75 % and 100 % and weighed after each stage. The time to attain equilibrium at each humidity was kept fixed at 24 h.

3. Results and discussion

The mixed phase hydrogel exhibited all the characteristics of a true gel. No visible separation of the individual constituents was observed on ageing. The mixed solution of the ingredients did not show any sign of hydrolysis and during slow addition of ammonia, hydrolysis occurred gradually and the whole system set to an enblock gel at pH 9. This was observed in all the samples having different mole ratios of $MgO:ZrO_2$ and this was related to the critical instability point of the system. The mixed hydroxide hydrogel possesses residual colloidal charge which was responsible for proper orientation of the polar water molecules in the gel structure. Proper gel formation was also ascertained through the release of synersis liquid after ageing. No special observation was noted regarding the consistency of the gel. At this particular pH interaction was almost complete according to the stoichiometry of the batch mixture and this was confirmed by testing the filtrate during washing. In order to avoid agglomeration, drying of the washed filtrate cake was carried out under vacuum.

The physical texture of the dried powder was semi-soft, white and homogeneous in nature. The physico-chemical characteristics of the dried precursor powder are given in Table 1. The purity of the samples was ascertained through chemical analysis. The mole ratio of $MgO:ZrO_2$ was found to be as per the batch mixture.

The loose bulk density was sufficiently low, which was characteristic of active precursor powder. This was found to be a direct function of ZrO_2 in the composition.

Table 1. Physico-chemical properties of mixed hydroxide hydrogel of MgO–ZrO$_2$ system.

Sl. No.	Properties	Sample Identity		
		Batch I	Batch II	Batch III
1.	Mole ratio MgO : ZrO$_2$	1 : 0.154	1 : 0.264	1 : 0.358
2.	DTA peak temperature (°C)	140, 390 (endothermic) 660 (exothermic)	105, 380 (endothermic) 630 (exothermic)	120, 358 (endothermic) 608 (exothermic)
3.	Specific surface area (m^2 g^{-1})	225	205	187
4.	Loose bulk density (g cm^{-3})	0.449	0.479	0.552
5.	Average particle size (μm)	24.60	25.80	28.81
6.	Infrared peak (cm^{-1})	3 698, 3 426, 2 368, 1 562, 1 388	3 699, 3 432, 1 560, 1 392	3 698, 3 424, 2 372, 1 561, 1 384
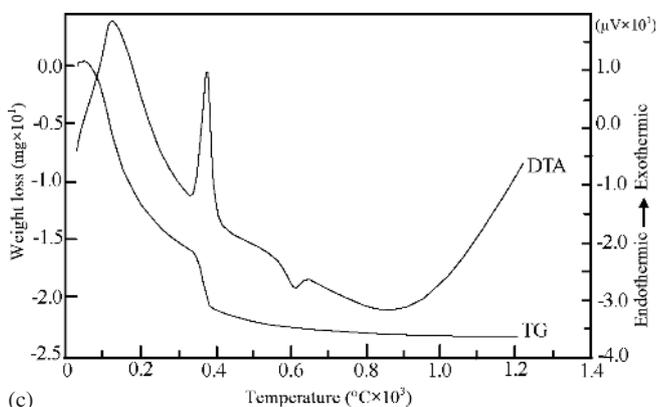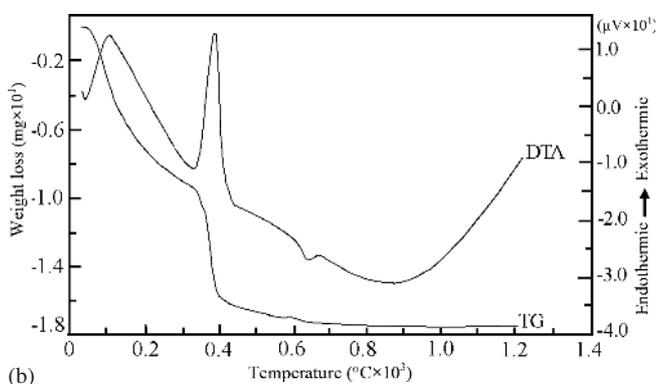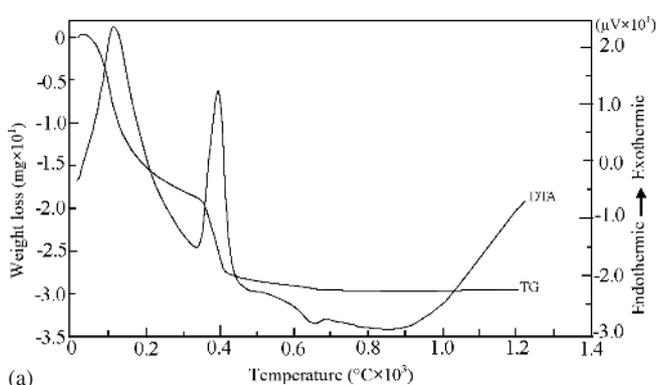
Fig. 1. Simultaneous DTA-TG plots for (a) batch I, (b) batch II and (c) batch III hydrogels. On progressive heat treatment of the hydrogel, dehydration and dehydroxylation occur at two distinct temperature regions. Batch composition influences the reaction temperatures.

DTA of the dried mixed hydroxide hydrogels was carried out in order to have an understanding of their thermal history in relation to the mole ratio of MgO : ZrO$_2$. The thermograms are shown in Fig. 1. Initial strong endothermic peak was due to the expulsion of loosely bound gel water. The peak temperature followed an inverse relation with the ZrO$_2$ content in the composition which might be due to the nature of water bonding in the secondary coordination of the respective hydrogel structure. Another strong endothermic reaction was noticed at higher temperature with all the samples and this was related to the dehydroxylation of the hydroxides. Here also the peak temperature exhibited the same sequence as stated earlier. A small exothermic peak above 600 °C might be due to crystallization of monoclinic ZrO$_2$ from the hydrogel lattice. There was distinct variation of the peak temperature with ZrO$_2$ content.

The surface area of the precursor powder was found to be significantly high. In this particular binary system the specific surface area decreased with increase in ZrO$_2$ content, which appears to be the result of particle agglomeration.

One of the important characteristics of the powder relating to sintering is the state of agglomeration. Bonding in agglomeration varies from weak forces, easily overcome by mechanical or hydrodynamic action to solid bridges as strong as a primary particle. Under dry conditions Van der Waals forces exist between the particles. The packing density of the loose powder or typical bulk density is low for fine powder. This is related to the state of agglomeration. Too low bulk density is undesirable for handling and forming as low bulk density allows only poor die fill; this will lead to granulation. Particle size distribution is one of the important considerations for the high temperature reaction. This was done for the three hydrogels and is shown in Fig. 2.

The infrared spectra of the three hydrogel powders are given in Fig. 3. The characteristic peaks did not shift significantly, thereby indicating that the physical identity of the individual hydroxide was always retained in the mixed system. The OH stretching vibration gives rise to a sharp band in the region 3 700 – 3 426 cm^{-1}. However, the stretching vibration in hydroxide is partnered by a bending vibration. Bent tri-atomic water molecules have three normal modes – the symmetric, the asymmetric and the bending vibrations. All these vibrations are IR active, but the symmetric and asymmetric stretching modes are not usually resolved in free and adsorbed water due to the effects of H-bonding. The broad peak in 3 699 cm^{-1} region was due to the OH
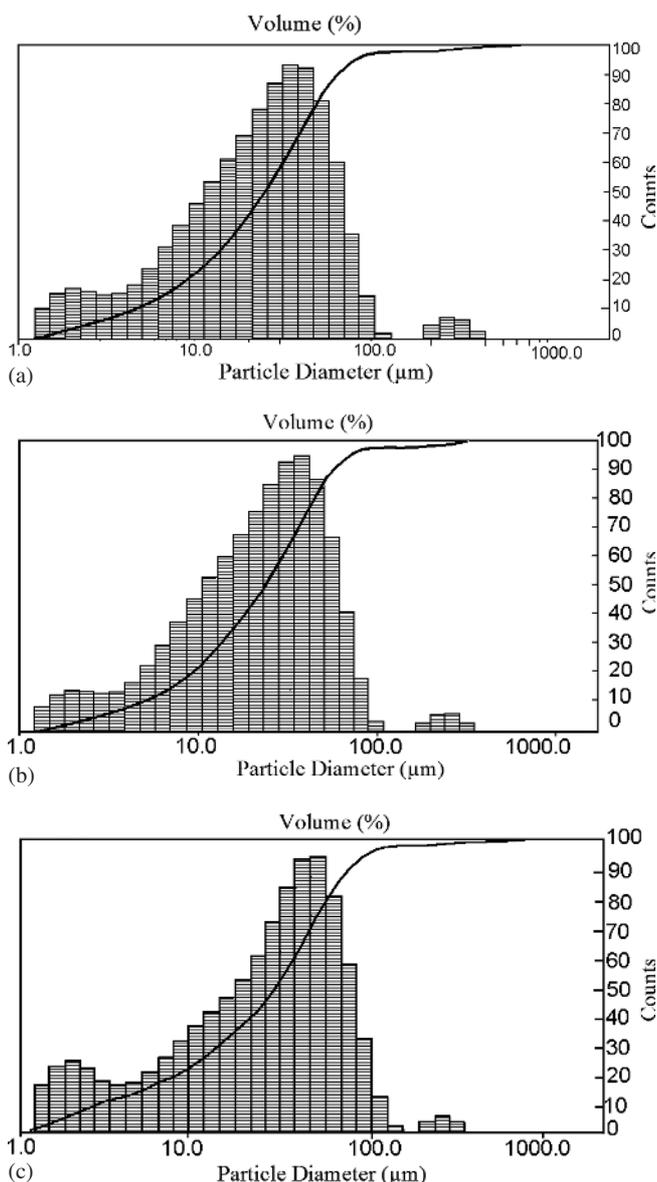
Fig. 2. Particle size analysis of (a) batch I, (b) batch II and (c) batch III. There is a clear trend of increasing average particle diameter and consequently reduction in specific surface area with the increase in ZrO₂ content in the batch composition.

stretching vibration in the gel structure. The aqueous gel contained a large number of entrapped water molecules and there may be also some H–H linkage. The frequency of this absorption band depends on the nature of the element to which the OH groups are directly bonded. The irregularities were indicated by the broadness and shallowness of the bands. The peak at 1560 cm^{-1} probably resulted from the coupling of H–O–H bending vibration. The Zr–O stretching vibration was indicated by the peak at 1390 cm^{-1}. The Zr–O vibrations are quite intense and therefore the peak shifted to its side. The Mg–O stretching vibration might be cancelled out by the anti-aligned bending vibration of Zr–O bond, as it was not observed in the spectrogram.

X-ray analysis was carried out to identify the presence of any crystalline phases in the precursor powder. The XRD analysis curves are shown in Fig. 4. Absence of any specific peak, either for MgO and ZrO₂ or for the composite system, clearly indicates the amorphous nature of the precursor powders.
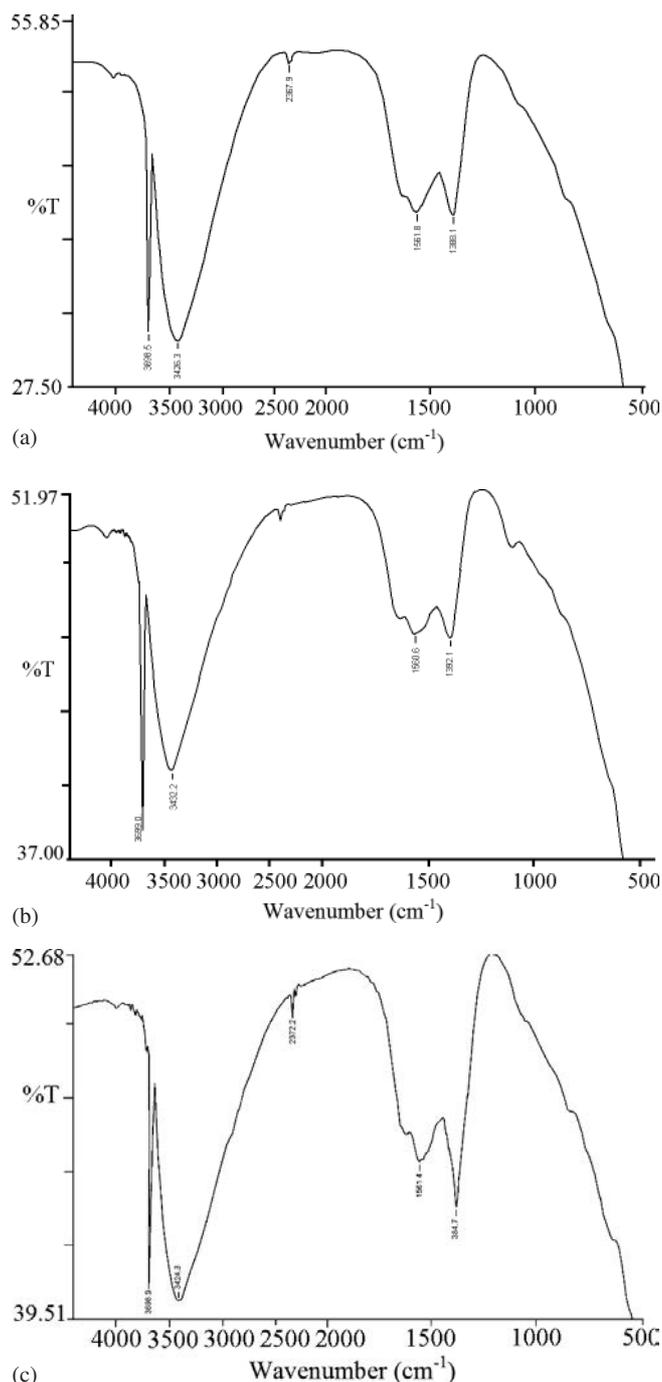

Fig. 3. Infrared analysis of (a) batch I, (b) batch II and (c) batch III. Insignificant shifts in the characteristic peaks of the individual oxides indicate that the identity of each oxide is retained in the composite hydrogel.

Morphological features of the dried mixed hydroxide hydrogel powder were examined through microstructural study. The SEM micrographs are shown in Fig. 5. These micrographs indicate the formation of amorphous material. Discrete small pores were also observed. The size, number, shape and location of these pores always change with thermal history.

The micrograph of batch I revealed irregular flake shaped aggregates which appeared to be stacking of units without regular outlines. Flake shaped units were sometimes too small to be seen individually, but in other cases they are discernible. More regularity in the distribution pat-
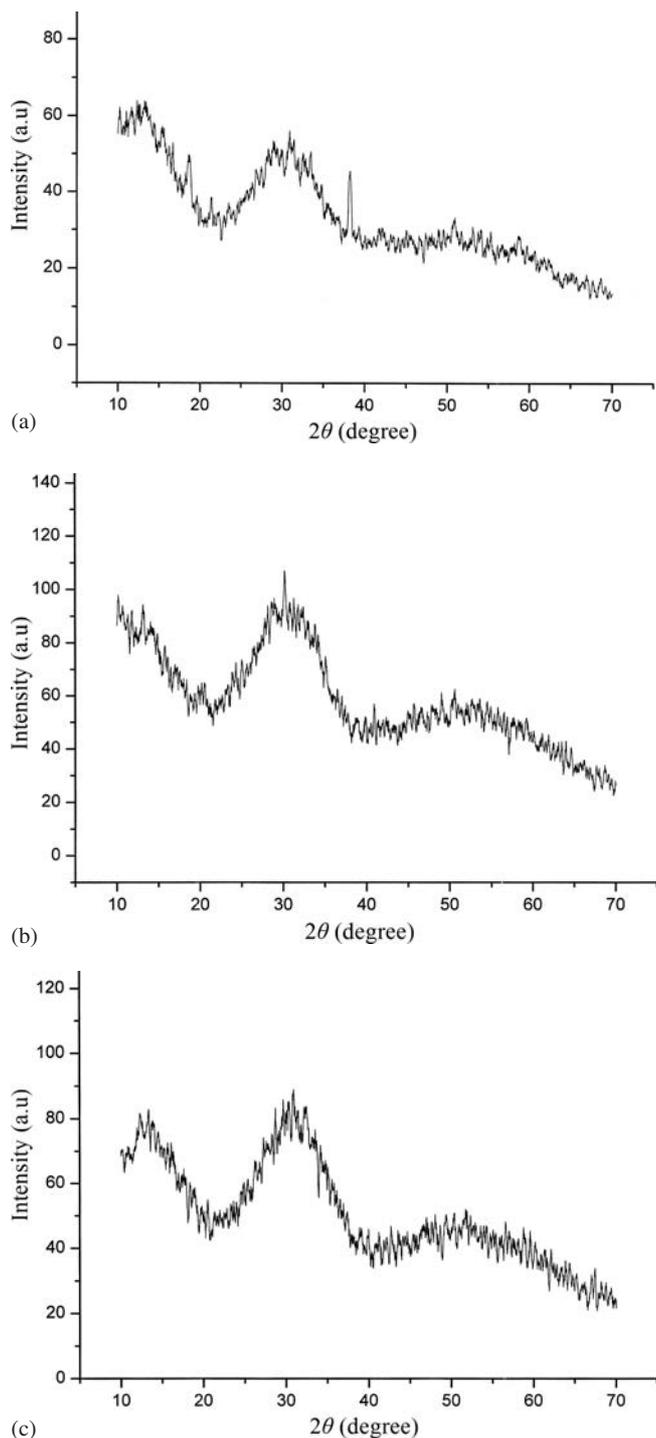
(a)

(b)

(c)

Fig. 4. X-ray analysis of (a) batch I, (b) batch II and (c) batch III. Complete amorphous nature of the hydrogels is supported by the absence of crystallization peaks.
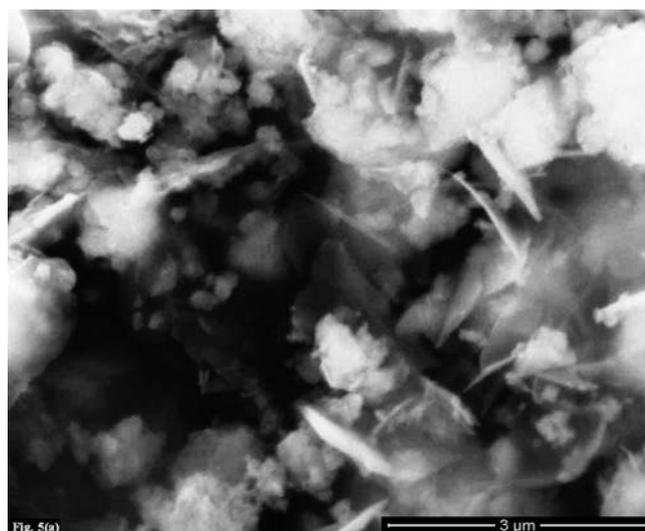

(a)

(b)

(c)

Fig. 5. Scanning electron micrographs of (a) batch I, (b) batch II and (c) batch III hydrogels. Presence of irregular flaky aggregates without properly developed outlines indicates the amorphous nature of the hydrogels. Brighter zirconium hydroxide particles are distributed in the matrix in a quasi-heterogeneous pattern.

tern was observed with batch II. Particles in general are smaller and zirconium hydroxides (brighter ones) were distributed in the matrix in a quasi-heterogeneous pattern. Batch III exhibited flaky aggregate with poorly developed outlines. The edges of the flakes were somewhat ragged and irregular. They occurred in thinner particles than batch II. The aggregate appeared to be composed of flake shaped units.

The micrographs of batch I exhibited the presence of fluffy aggregates in the matrix. Here there was always a distinct tendency towards elongated lath shaped units. It was
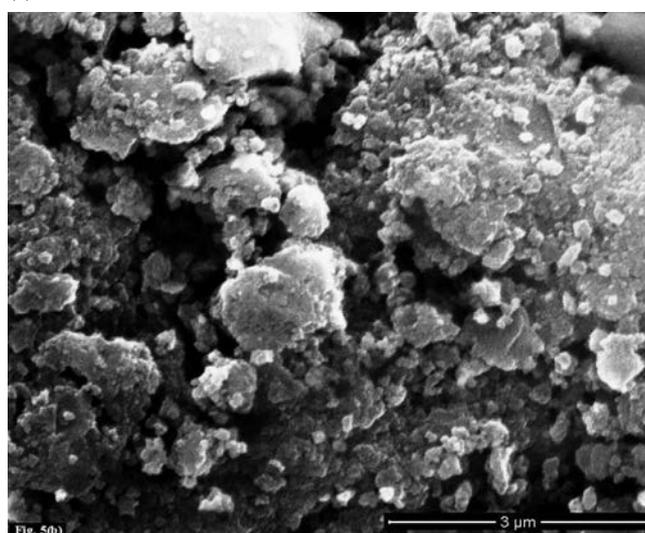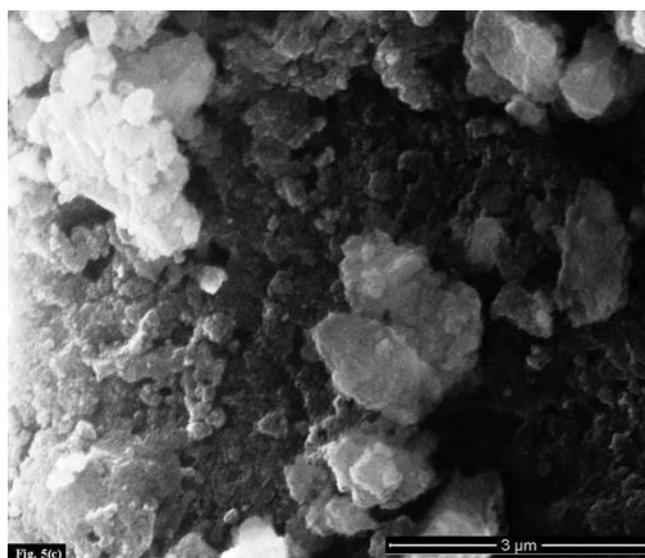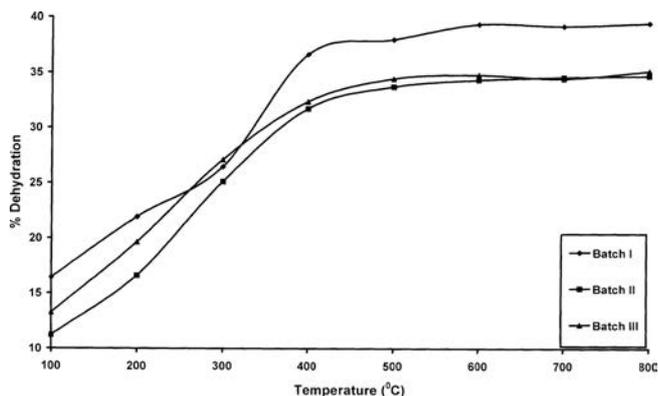
Fig. 6. Relationship between percent dehydration and temperature. The dehydration process follows a discontinuous path and is independent of the batch composition. Initial fast rate of dehydration slows down during progressive heat treatment.

found from the distribution of phases that Zr(OH)$_4$ particles were in general smaller than Mg(OH)$_2$ particles.

Most of the properties related to the gel activity have been associated with the amount and orientation of water molecules. All the hydrogels were subjected to equilibrium dehydration which actually involves loss of water from mixed hydroxides that are bonded to the gel network probably in a heterogeneous manner. In this type of hydroxide hydrogels there are two types of water. Gel water which is attached with fairly loose bonding, is expelled at low temperature. The other is constitutional water which is strongly bonded to the cations.

The nature of the dehydration curves (Fig. 6) appears to be more or less identical irrespective of the of the variation of mole ratio of MgO : ZrO$_2$. From an analysis of the above relationship it has been observed that the whole course of dehydration followed a discontinuous path. Up to 400 °C dehydration proceeds at a faster rate and exhibits an inflection, following which it slows down up to the final temperature of heat treatment. The structure of these colloidal gel particles normally corresponds to that of the bulk solid of the same composition. The pores here are larger than in polymeric gels and as such capillary stress develops during the removal of liquid from the pores in the earlier temperature range of the heat treatment. Thus the structure of the heat treated gel at this region is characterized by large porosity and this has important consequences for the firing of the dried gel.

In case of amorphous materials, when dehydration starts the temperature of the surface of the gel drops because of the loss of heat due to latent heat of vaporization of the liquid. However, heat flow to the surface from the atmosphere quickly establishes thermal equilibrium where heat transfer to the surface balances heat loss due to latent heat of vaporization.

The network becomes stiffer with the increase in temperature because of the formation of new bonds by condensation reaction and the porosity decreases.

Rehydration of the hydrated hydrogel is normally related to the structural flexibility and the hydration affinity of the individual phases. The dehydrated sample at each temperature was subjected to rehydration successively at four different humidities. The magnitude of rehydration was calculated on the basis of dehydrated weight. The rehydration–temperature relationship with variation of humidity is shown in Fig. 7. The nature of the curves did not differ to a
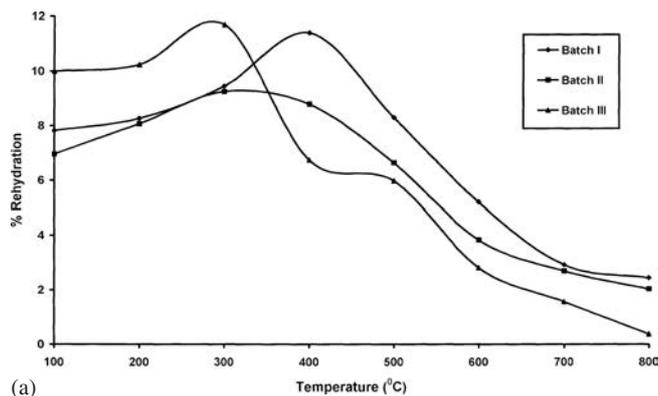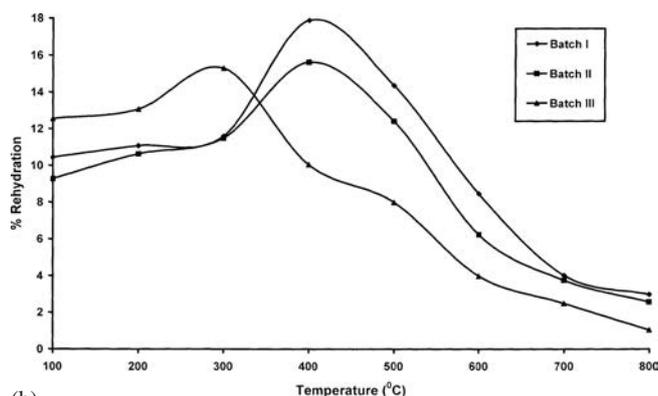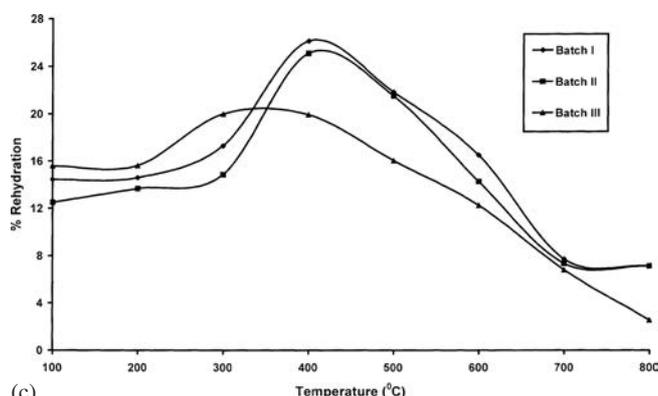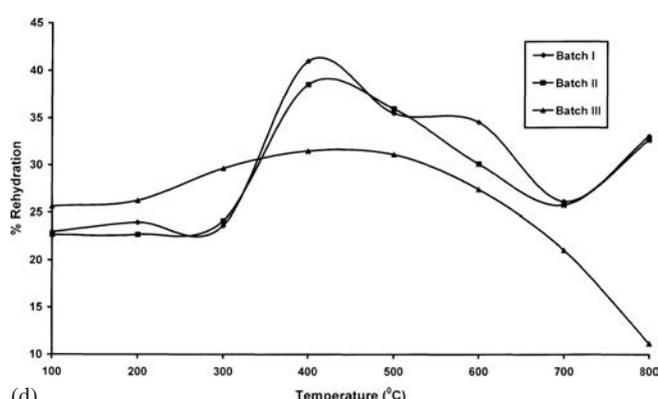

Fig. 7. Relationship between percent rehydration and temperature at (a) 33 %, (b) 55 %, (c) 75 % and (d) 100 % relative humidity. Change in powder morphology on progressive heat treatment and mechanism of rehydration are independent of batch composition. The discontinuous nature of rehydration curves is attributed to collapse of the gel structure after a threshold limit during dehydration.

great extent, only the magnitude of adsorption followed a direct relationship with humidity. This clearly indicates that the morphological change of the hydrogel structure as well as the mechanism of water adsorption remained unaltered. The magnitude of rehydration initially increased reaching a maximum at the temperature range of 300–400 °C and then decreased up to the final temperature of heat treatment. The initial increase in moisture adsorption was due to release of air by thermal excitation, resulting in a slight increase of pore volume. At the later stage, the gel structure collapsed due to the heat treatment after the threshold limit leading to a decrease in rehydration. In case of batch III, the peak was shifted to 300 °C, which might be related to compositional change.

When the oxide surface gets completely dehydrated it tends to become hydrophobic. During cooling to room temperature rehydration was slow even though it was favoured thermodynamically.

Without surface OH groups, water molecules come back to surface sites forming hydrogen bonding and therefore physical adsorption of water was difficult.

Initially, the rehydration rate followed a certain course irrespective of composition up to 75 % RH following which it changed. Sharpness of the peak was found to be both composition and humidity dependent. The reversibility of dehydration–rehydration was found to be related to the structural stability which was maintained up to 300 °C due to retention of the amorphous nature of the hydrogel. Along with physical adsorption, some reconstitution of OH groups might occur, thereby changing the surface characteristics.

4. Conclusion

The synthesis of precursor powder via a wet interaction process inculcated several advantageous properties in the powder which could be tailored to produce materials for specific application. The powder exhibited high purity and homogeneity. Very high specific surface area of the powder suggested its poor agglomeration tendency. X-ray and SEM studies indicated the formation of amorphous powder in all the batches, and zirconium hydroxide and magnesium hydroxide were found to be distributed quasi-heterogeneously. Equilibrium dehydration–rehydration curves were found to be independent of the mole ratio of the constituents. Change in powder morphology on progressive heat treatment and the mechanism of rehydration were almost identical in all batches. Though all three batches of the MgO : ZrO₂ composite system followed a discontinuous path during both dehydration and rehydration, the magnitudes were clearly dependent on temperature and humidity.

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