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Kinetics of thermal dehydration of sol-gel derived MgO–ZrO$_2$ composite hydrogel

The kinetics of thermal dehydration of mixed hydroxide hydrogels in MgO–ZrO$_2$ system was studied as a function of composition by following the isothermal heat treatment route. Kinetic parameters were calculated through the application of the Guggenheim equation. The expulsion of both loosely bound water and constitutional OH groups were not continuous processes but proceeded in steps. The applicability of 1st order reaction kinetics for the major portion of the reaction for all compositions suggests that during the dehydroxylation process the dehydration is essentially controlled by the orientation of H$_2$O molecules and the mutual interaction of hydroxyl groups. Due to a decrease in the concentration of the reacting species the activation energy was always higher at the final stage of dehydration.

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

1. Introduction

Water in various forms appears to be an integral part of a gel structure. Due to heterogeneity in bond characteristics expulsion of water does not follow a single mechanism. Moreover, expulsion leading to conversion to the oxide state has a strong influence on the particle morphology as well as orientation leading to agglomeration. Most of the important properties of the synthetic hydrogel are related to the magnitude as well as orientation of the water molecules.

In endothermic solid state reaction, the dissociation and recombination processes occur simultaneously causing complications both in the experimental technique and theoretical interpretation of the results. The most useful experimental method for the study of such systems is the weight loss method where the reaction is followed on a microbalance. Generally, two factors determine the dehydration rate;

(i) The rate of loss of water formed by the interaction of OH groups from the interface between the hydroxide and the products

(ii) The rate of diffusion of water molecules through the solid product

Since diffusion has only a small temperature coefficient, there is relatively less impedance to the escape of water vapor due to diffusion at low temperature [1]. Kinetic study was therefore performed using isothermal dehydration experiments under identical condition. Butt et al. [2] studied the kinetics of thermal dehydroxylation of Mg(OH)$_2$ using isothermal and non-isothermal thermogravimetric analysis (TGA) and concluded that Mg(OH)$_2$ undergoes rapid dehydroxylation and subsequent phase transformation at 375 °C. Halikia et al. [3] used four different methods of isothermal kinetic analysis to determine the mechanism of magnesium hydroxide decomposition and concluded that the nucleation mechanism predominates in the Mg(OH)$_2$ decomposition at all experimental temperatures. L'vov et al. [4] proposed the mechanism of thermal dehydroxylation of Mg(OH)$_2$ as dissociative evaporation of Mg(OH)$_2$ in the form of MgO and H$_2$O molecules. Experimental values of the rate of decomposition and activation energies are found to be in agreement with theoretical calculations. Hartman et al. [5] employed both increasing and constant temperature gravimetric methods to measure the rates of decomposition of Mg(OH)$_2$ and Ca(OH)$_2$ between 290–430 °C. The results were tested empirically by fitting to the nth order rate equation of Arrhenius type and the values of the kinetic parameters were estimated. Gusmano et al. [6] hypothesized the mechanism of the formation of MgAl$_2$O$_4$ spinel powder from thermal decomposition of co-precipitated hydroxide mixtures.

The thermal decomposition of zirconium hydroxide was also studied by several researchers. Cypries et al. [7] studied the differential thermal analysis (DTA) of zirconium hydroxide and found a broad endothermic peak between 175–300 °C and a sharp exothermic peak at 405 °C. They concluded the latter reaction as being due to the transformation of amorphous zirconia to tetragonal form. According to Livage [8] the explosive crystallization to tetragonal form appears at 430 °C. However, Selim et al. [9] suggested that the exothermic peak at 460 °C was due to transformation of zirconium oxyhydroxide to amorphous oxide and then a part of it transforms to a metastable form giving rise to the exotherm at 540 °C. In contrast, some researchers suggested the 460 °C isotherm as due to crystallization of amorphous zirconia to monoclinic form. Sato et al. [10] suggested that the transformation of amorphous zirconia to either monoclinic or metastable tetragonal form depends on the original starting material. They also concluded from thermogravimetric analysis that the dehydration of zirconium hydroxide continues even at 400–600 °C. The kinetics of the dehydration of zirconium hydroxide under hydrothermal condition (200–400 °C) was studied by Nekrasov et al. [11]. They found that the dehydration rate was related to the temperature and duration of the experiment. Two metastable phases were formed and rapid dehydration occurred at 200–400 °C.

The isothermal dehydration kinetics of synthetic zeolite (in different cationic forms) is a low energy diffusion controlled process following 1st order kinetics for the major part of the reaction. Exchangeable cations were found to influence the kinetic parameters of the dehydration process [12]. Mitra et al. [13] studied the kinetics of thermal dehydration in the synthetic hydrogel of $ZrO_2 \cdot Al_2O_3 \cdot SiO_2$ system. The non-crystalline hydroxide hydrogel was synthesized via wet interaction in the aqueous phase where the identity of individual hydroxides was retained. The major portion of the dehydration curve was found to follow 1st order kinetics. Phase transformation in the composite powders of alumina and zirconia was examined by Balasubramanium et al. [14]. The composite powders were initially amorphous and crystallization began at 900 °C. Because of the fine particle size and the constraints imposed ZrO_2 was retained in tetragonal form.

Bielanski and Tompkins [15] have studied the sorption of water vapor on single crystals of dehydrated potash alum and pointed out that rehydration is influenced by

(i) Reversibility of the absorbed water and
(ii) The secondary absorbed water which is absorbed irreversibly

An excellent review of the kinetic process involving solids has been given by Garner [16]. He classified reactions involving solids as diffusion controlled compared to reaction controlled. The effect of vapor pressure on the rate of decomposition of salt hydrates has also been investigated by a number of authors [17–19]. They explained that at low water vapor pressure a very fine amorphous structure with narrow capillaries is formed during decomposition. The rate of passage of water vapor is necessarily low. As the vapor pressure increases, adsorption of water vapor decreases the rate.

The decomposition kinetics of alumino-silicate hydrogel was found to follow formal first order kinetics [20]. The activation energies showed little variation with particle size which was attributed to the highly porous structure of the hydrogel.

The present investigation was undertaken to study the kinetics of thermal dehydration of the mixed hydroxide hydrogel of MgO–ZrO₂ system under isothermal condition using the Arrhenius relationship. The kinetic parameters act as a guide in determining the sinterability, physicochemical and electronic properties of the composite. The structural and surface characteristics and the physico-chemical properties of the subject composite can be tailored by varying the reactant mole ratio to cater to its various applications such as catalysis, chromatographic packing, solid electrolyte etc. [21, 22].

2. Experimental procedure

2.1. Synthesis of the mixed hydroxide hydrogel and analysis

Three hydrogels of the MgO–ZrO₂ composite system with varying MgO : ZrO₂ ratios were prepared via wet interaction in the aqueous phase [23, 24]. Both the ingredient salts viz., $Mg(NO_3)_2$ and $ZrOCl_2$ were of analytical grade and water soluble with least tendency to hydrolyze. Aqueous solutions of the salts were prepared by dissolving in deionized water. The individual salt solutions were mixed in requisite volumes to prepare three solution mixtures based on the intended composition of MgO : ZrO₂ in the precipitated hydrogel. In each case the solution concentration was adjusted to 5 % w/v by adding deionized water. The hydroxides were precipitated from the solution on addition of excess 1 : 1 ammonia with constant stirring and the whole mixture set into an enblocked gel at pH 9. The set gel was allowed to age for 24 h, whereby syneresis occurred indicating perfect gel formation. The aged gel was washed repeatedly with deionized water until the settled mass showed the tendency to disperse. The hydrogel was then filtered through a Buckner funnel, washed with hot deionized water until flocculation was visible on addition of silver nitrate to the filtrate, and finally dried under vacuum at 50 °C.

Chemical analysis of all three hydrogels was carried out to ascertain the mole ratio of MgO : ZrO₂ in the composite hydrogels (Table 1) while the thermal history of the hydrogels was studied through differential thermal analysis (DTA) [24].

2.2. Dehydration kinetics study

The rate of dehydration of the powdered sample was ascertained through isothermal dehydration experiments carried out in a thermo-gravimetric apparatus. About 0.5 g of accurately weighed sample was taken in a platinum crucible and suspended into the uniform firing zone of a tubular furnace through one arm of a thermo-balance. The tip of a thermocouple was placed very close to the crucible and was maintained at fixed position. The temperature of the furnace was raised and controlled by an adjustable resistor to restrict the variation in temperature rise within ± 0.5 K. In each experiment same weight of the sample was taken and spread to the same thickness in the crucible. The samples were equilibrated at 32 ± 1 °C every time before experimentation. The weight loss was recorded at suitable time intervals and the initial weight corresponding to zero time being taken from the instant of suspension of the crucible inside the furnace. The need for buoyancy correction for the weights of the iso-

Table 1. Physico-chemical properties of mixed hydroxide hydrogel of MgO–ZrO₂ system.

Sl. No.	Properties	Sample Notations		
		Batch I	Batch II	Batch III
1	Mole ratio of MgO–ZrO₂	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)

thermal dehydration is obviated in all cases. During isothermal dehydration study at higher temperature zones (dehydroxylation) the samples were preheated at 200 °C to remove the gel water completely so that it would not affect the kinetics of dehydroxylation.

3. Calculation

The dehydration of the experimental hydrogel proceeded in two steps (Fig. 1a–c). The initial strong endothermic peak was due to the expulsion of loosely bound gel water while the other strong endothermic peak at higher temperature was related to the dehydroxylation of the hydroxides. A small exothermic peak above 600 °C might be due to crystallization of monoclinic ZrO$_2$ from the lattice. The plots of weight loss against time (Fig. 2a–c) indicate the exponential nature of the dehydration process and thereby suggesting the applicability of first order kinetics. The rate of loss of water from the sample would be proportional to the concentration of water present in the sample at that stage. Again the weight of water present in the sample that is lost at the experimental temperature, when divided by the volume of the sample, will be equal to the concentration of water in the sample. Therefore, the concentration term may be replaced by the relevant weights if the weight, and hence the volume, of the sample is kept fixed.

Thus at a specified temperature if

L = Loss of weight at time t and

L_∞ = Total weight loss at infinite time

then L_∞ is equivalent to the initial concentration of water in the sample (dehydratable at the experimental temperature) and $(L_\infty - L)$ is equivalent to the concentration of water remaining in the sample at time t. Hence, according to the first order kinetics, the rate of loss of water will be given by

$$\mathrm{d}L/\mathrm{d}t = k(L_\infty - L) \quad \text{or}$$

$$\log[(L_\infty - L)/L_\infty] = -kt/2.303 \tag{1}$$

Equation (1) permits establishing the rate constant (k) for dehydration from the slope of the line obtained by plotting log $[(L_\infty - L)/L_\infty]$ against t, provided the value of L_∞ is known. Since, theoretically, first order reaction never goes to completion, all direct methods of determining L_∞ would be erroneous and as such have not been attempted. Instead the method originally suggested by Guggenheim has been adapted for the evaluation of both L_∞ and k.
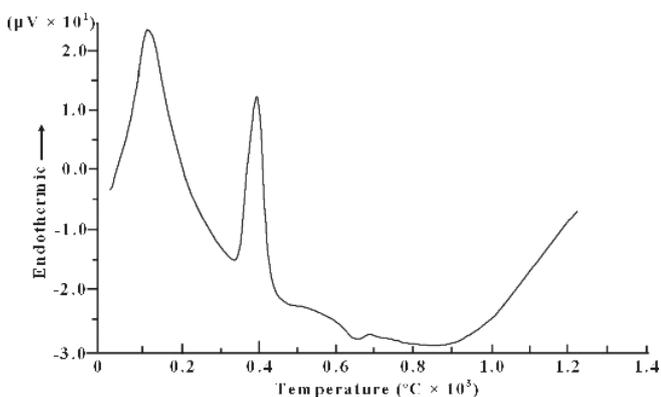
Let $L_1, L_2, \ldots L_n$ be the weight losses at the time $t_1, t_2, \ldots t_n$ and let $L_1', L_2', \ldots L_n'$ be the losses at time $t_1 + \mathrm{d}t, t_2 + \mathrm{d}t, \ldots t_n + \mathrm{d}t$ i.e., the set of readings L' was taken at constant time interval $\mathrm{d}t$ after the previous set L. By using Eq. (1) we can write
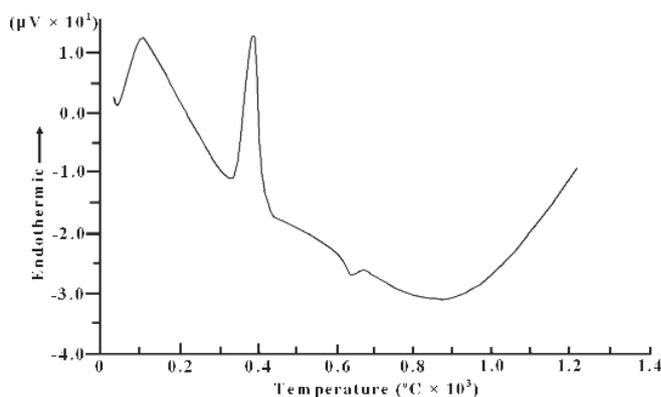
$$L_\infty - L = L_\infty \exp(-kt_1) \quad \text{and}$$

$$L_\infty - L_1' = L_\infty \exp[-k(t_1) + \mathrm{d}t)]$$
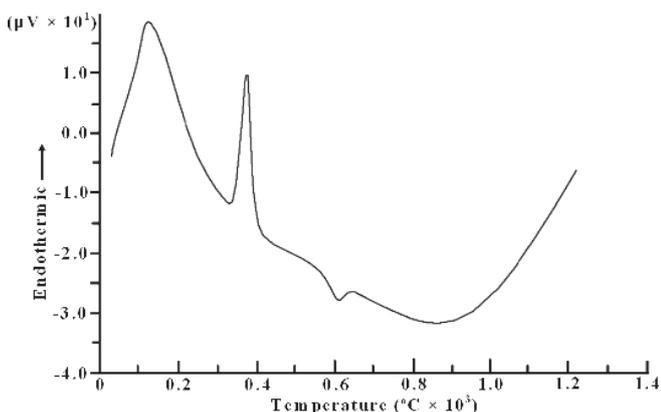
subtracting

$$L_1' - L_1 = L_\infty \exp(-kt_1)][1 - \exp(-k\mathrm{d}t)]$$


(a)

(b)

(c)

Fig. 1. Differential thermal analysis of (a) batch I, (b) batch II and (c) batch III hydrogels. Initial strong endothermic peak was due to expulsion of loosely bound gel water. The other endothermic peak at higher temperature resulted from the expulsion of OH groups from hydroxides of both cations.

Taking the logarithm and putting dL for $L_1' - L$ terms, the equation takes the general form

$$\log dL = (kt/2.303) + \log L_\infty[1 - \exp(-kdt)] \qquad (2)$$

where dL is the difference between the weight loss at time $t + dt$ and that at time t. The time interval dt between the two sets of readings being fixed at a value greater than twice the time for 50 % dehydration. Using Eq. (2) the rate constants can be calculated from the slope of the straight line obtained by plotting log dL against time t. Knowing dt and having obtained k from the slope, L_∞ can be determined from the intercept of the line on the log axis. The extent of
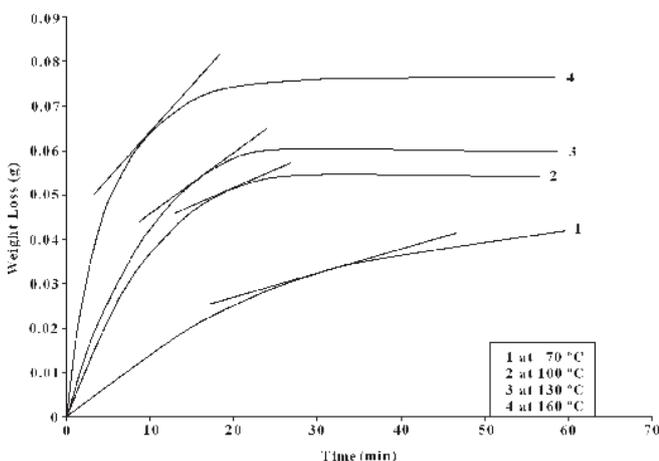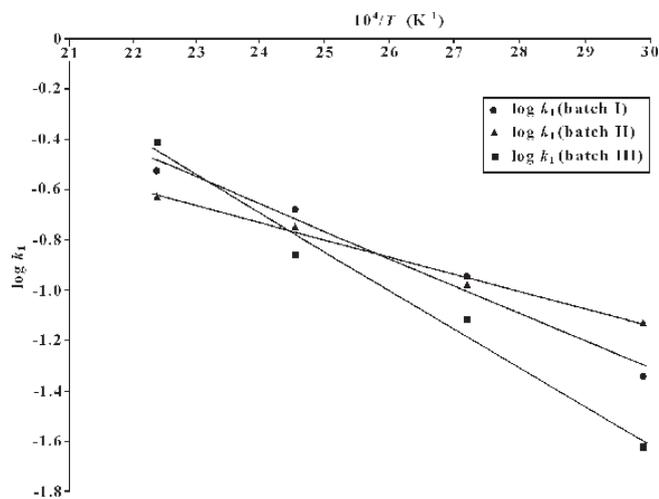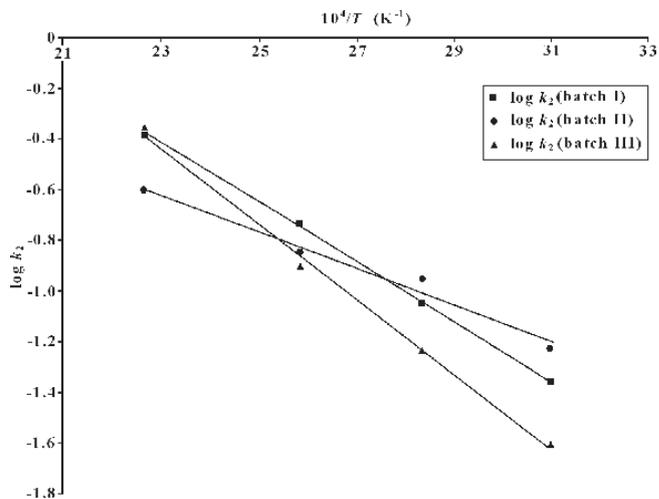

(a)
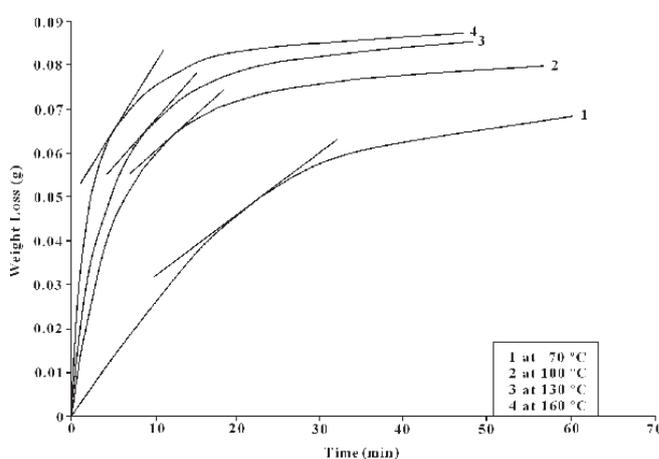
(b)
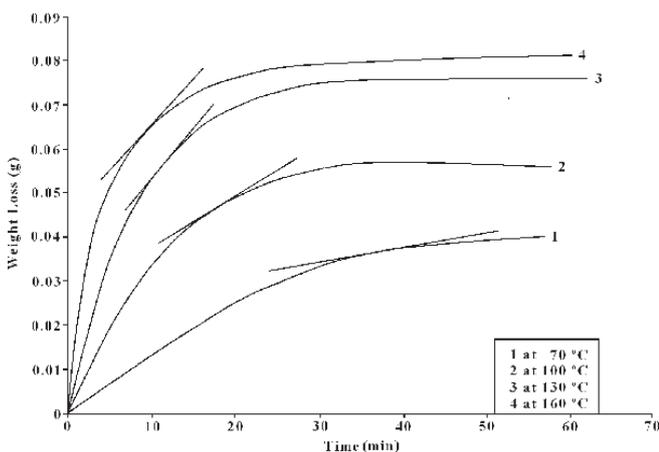
(c)

Fig. 2. Weight loss against time plots for gel dehydration of (a) batch I, (b) batch II and (c) batch III hydrogels. The exponential nature of the curves indicated first order kinetics. However, the whole course of reaction was not uniform. The applicability of first order kinetics ceases after a certain point, as evident from the flattening of the rate curves.

(a)

(b)

Fig. 3. Plots of log k against $1/T$ for (a) initial and (b) final stages of dehydration. The mean curve obtained by fitting the experimental data was a straight line. The batch composition of the hydrogel influences the activation energy.

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validity of the first order kinetics can be obtained by plotting log $(L_\infty - L)/L_\infty$ against time using calculated values of L_∞.

In the later stage of dehydration, though the reaction does not follow first order kinetics, the rate of dehydration would still be proportional to the concentration of remaining H$_2$O molecules. The rate constant k_2 for the final stage of dehydration was calculated from the relation

$$k_2 = (\mathrm{d}L/\mathrm{d}t)/(L_\infty - L)$$

where $\mathrm{d}L/\mathrm{d}t$ is the slope of the weight loss against time curve at the point of dehydration beyond which first order kinetics was not followed.
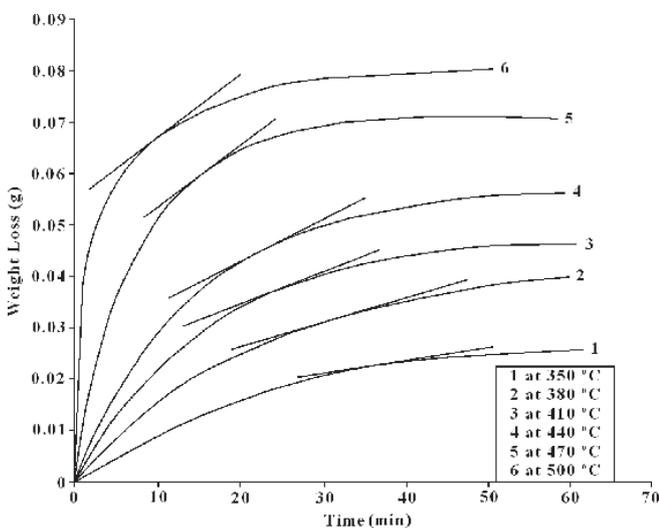
Finally, the values of reaction rate constant at both stages were used to draw the Arrhenius plot i. e., log k against $1/T$ (Fig. 3a and b). From the slope of these curves activation energy (E) was calculated in accordance with the well known equation

$$\log k = E/4.576T$$

Where T indicates absolute temperature.
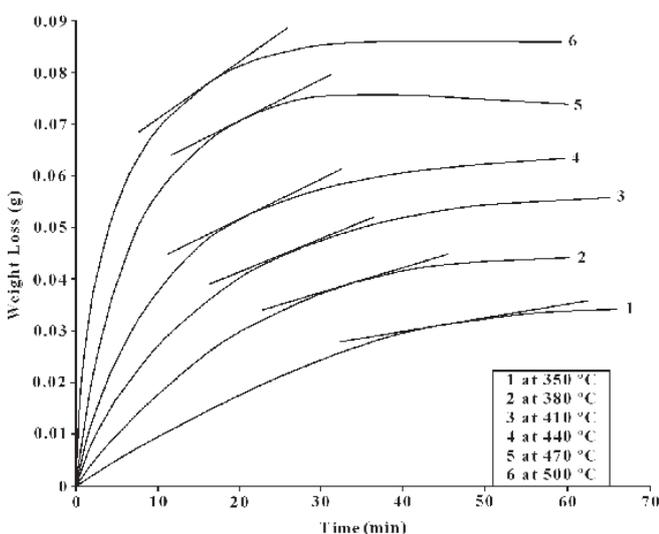
The plots of weight loss against time for dehydroxylation reaction (Fig. 4a–c) also exhibit an exponential nature and thereby suggest the applicability of first order kinetics. The values of the reaction rate constants, L_∞ and extent of validity of first order law were calculated following the same method. Activation energy was calculated using Arrhenius plots (Fig. 5a and b).

4. Results and discussion

The weight loss in the first stage of dehydration (first endothermic peak in DTA curve) was due to desorption of physically combined gel water. In the next phase of thermal excitation, water gets removed as a by-product of the poly-condensation reaction whereby the hydroxides are transformed to corresponding oxides. The process involves transport of matter and is thus limited by the kinetics of the process.

The synthetic hydrogels possess a highly porous structure irrespective of the molar ratio of the constituents. During dehydration water molecules are expelled from both external and internal surfaces giving a dehydrated ionic

(a)

(b)
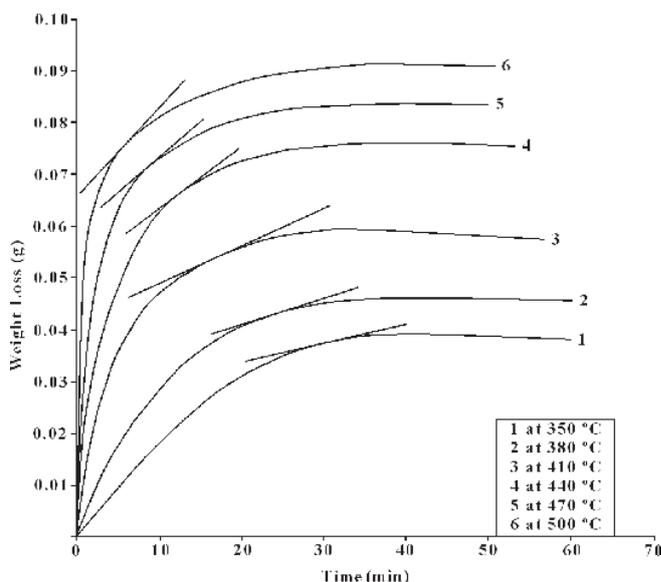
(c)

Fig. 4. Weight loss against time plots for dehydroxylation of (a) batch I, (b) batch II and (c) batch III hydrogels. The applicability of first order kinetics was evidenced by the exponential nature of the curves. The reaction does not follow first order kinetics consistently throughout the entire dehydroxylation process.

network which is fairly stable [25]. The structure of this intermediate ionic lattice depends on the molar ratio of the constituents and as such no single data point can generalize the whole process.

The experimental gel samples vary in their empirical formula and thus in water content, surface area and DTA peak

(a)

(b)

Fig. 5. Plots of log k against $1/T$ for (a) initial and (b) final stages of dehydroxylation. The mean curves for individual batches were straight lines. The activation energy values are higher for dehydroxylation reaction due to the ordered orientation of water molecules through primary coordination.
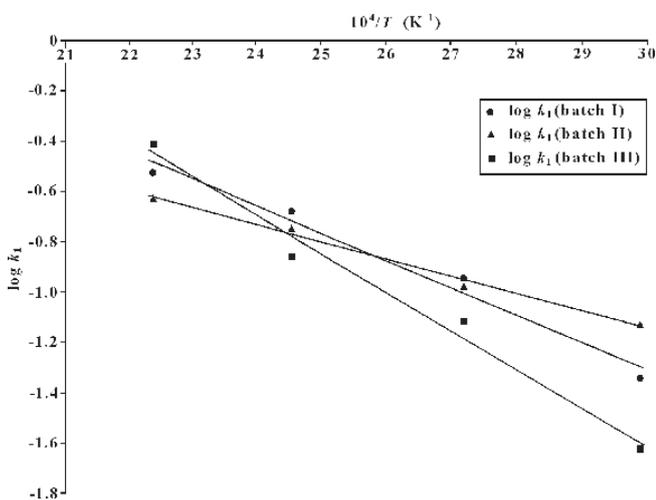
temperature [24]. These might influence the kinetics of dehydration.

The first stage of the kinetic study was performed according to the first DTA peak i.e., the expulsion of loosely bound water. The calculated values of reaction rate constant k_1 (min^{-1}) and total weight loss at infinite time L_∞ (g) are presented in Table 2. The rate constant values followed an inverse relationship with ZrO$_2$ content in the composition up to 130 °C. The faster increase in the reaction rate constant with temperature during early stage of dehydration may be explained in that the gel water is weakly bonded through Van der Waal's forces. There is also hydrogen bonding in the attachment of surface water. The positive temperature coefficient of k_1 values was a true indicative of endothermic reaction.
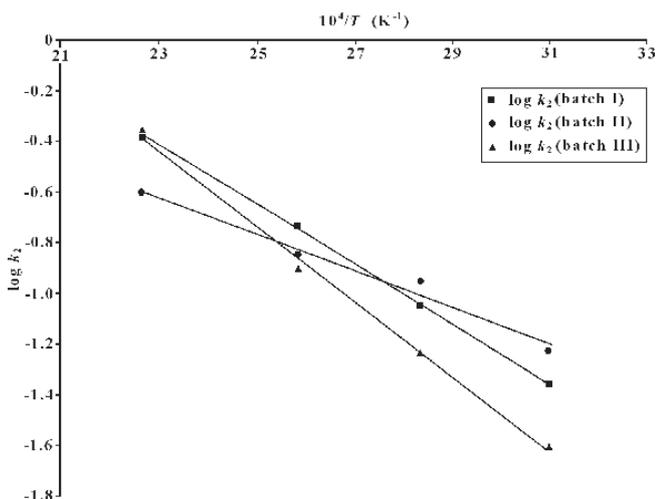
The equilibrium water content, i.e., L_∞ values, were found to be a direct function of temperature and also influenced by the molar ratio of the precursor powder. This clearly revealed that the cage house structure of the gel network for holding the polar water molecules is related to the orientation. Maximum value of L_∞ with batch III at 160 °C and minimum with batch II indicate that the cage house structure of the gel network for holding the charged water molecules required an optimum molar ratio of MgO : ZrO$_2$.

It was evident from the nature of the rate curve that the whole course of the reaction was not uniform and as such it was necessary to know how far the first order law is valid for this endothermic reaction. The calculated values of the extent of validity of first order law are given in Table 2. It may be concluded from the results that the extent of validity of first order law for gel dehydration was a direct function of temperature. Thermal diffusivity also appears to be an important contributory factor for this reaction. Among three batches, the maximum value was achieved with batch II. It is interesting to note that when the L_∞ value was minimum, the rate of reaction was relatively slow. Thus, the thermal dehydration in the synthetic hydrogel was not a continuous process and the last portion of water was lost at a rate which was completely different from that prevailing at the earlier stage of dehydration, as reflected through the flattening of the rate curves. However, the rate of dehydration at this stage would still be proportional to the concentration of the water molecules present in the system. The reaction rate constant for the later part of the reaction (k_2) are given in Table 3. The overall relationship was identical to that of k_1 values but k_2 values were always lower than the corresponding k_1 values.

From the general concept of reaction kinetics in heterogeneous systems it was quite clear that after the expulsion

Table 2. Values of reaction rate constant k_1 (min^{-1}), L_∞ (g) and extent of validity EV (%) of first order law for gel dehydration at different temperatures.

Temperature (°C)	Batch I (MgO : ZrO$_2$ = 1 : 0.15)			Batch II (MgO : ZrO$_2$ = 1 : 0.25)			Batch III (MgO : ZrO$_2$ = 1 : 0.35)		
	k_1	L_∞	EV	k_1	L_∞	EV	k_1	L_∞	EV
70	0.0550	0.0420	40.82	0.0782	0.0318	53.76	0.0552	0.0344	38.01
100	0.1230	0.0606	46.90	0.1456	0.0406	57.52	0.1034	0.0476	44.92
130	0.1963	0.0649	52.54	0.1701	0.0480	62.13	0.1190	0.0665	48.32
160	0.2519	0.0762	62.02	0.2237	0.0519	64.22	0.2610	0.0795	56.29

of bulk water from the gel structure in the earlier stage, the concentration decreased significantly, which hinders the mass transfer. Moreover, the dehydrated phase as generated caused a barrier to the escaping H$_2$O molecules and the porosity created in the residual mass decreased the rate of heat transfer. 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.

The activation energy values for these two different rate reactions were calculated using the Arrhenius equation and are presented in Table 4. Both E_1 and E_2 values were related to the nature of bonding of water molecules. The general observation was that E_2 values were always higher than E_1 values indicating lesser resistance to diffusion paths of the escaping H$_2$O molecules at the initial stage of dehydration. This can only be achieved by the formation of defects during lattice shrinkage exposing greater numbers of reaction sites. These factors overcome the difference in the forces of attraction of residual H$_2$O molecules at the initial stage of dehydration. With highest ZrO$_2$ content, activation energies exhibited highest values both at the initial and final stages of dehydration. Lowest values were exhibited by

batch II which might be related to the textural factors and subsequent generation of flaws within the gel structure.

Applying the similar concept of kinetics in heterogeneous reactions, experiments were conducted for the peak corresponding to the dehydroxylation of hydroxides of Mg^{2+} and Zr^{4+}. The reaction rate was found to follow 1st order kinetics at the initial stage. Reaction rate constant (k_1) and L_∞ values for the dehydroxylation process are given in Table 5. The rate of dehydroxylation was determined by the same factors operative during the dehydration process. The values of k_1 and L_∞ followed the same trend with temperature as in the dehydration process. k_1 values exhibited a direct relationship with ZrO$_2$ content in the composition and were also influenced by the dehydroxylation temperature of the individual hydroxides. L_∞ values were higher than those obtained in the low temperature zone (dehydration process). Thus it can be inferred that the hydroxyl content in the mixed gel was higher than for loosely bound gel water. In this case also batch II exhibited the lowest values while the maximum L_∞ values were observed with batch III. This might be due to some specific orientation of water molecules at an optimum molar ratio of MgO : ZrO$_2$.

The extent of validity of the 1st order law for dehydroxylation process was calculated in a similar manner as done for the dehydration process and is presented in Table 5. From the calculated values it was found that the extent of validity was greater compared to gel dehydration. More than 80 % reaction followed 1st order kinetics. This might be explained in the way that bonding of hydroxyl water was more uniform and it was always through primary coordination, whereas in the case of gel water more irregularities were expected due to the presence of some H$_2$O molecules in secondary coordination. The temperature effect was also found to be positive. In this particular study, the compositional effect was minimum as compared to the previous results.

In the dehydroxylation process k_2 values (presented in Table 6) were also lower than the corresponding k_1 values. Unlike the process of removal of loosely bound gel water, during dehydroxylation the tendency of reconstitution of OH groups to the dehydrated structure was comparatively low under normal conditions. The activation energy for the dehydroxylation process was higher than for expulsion of the gel water which was in conformity with the bond strength. E_2 values (Table 7) were higher indicating minimum irregularities in the dehydroxylated meta-stable structure.

Table 3. Values of reaction rate constants (k_2 in min^{-1}) at the final stage of dehydration

Temperature (°C)	Batch I	Batch II	Batch III
70	0.0330	0.0575	0.0342
100	0.0897	0.1294	0.0826
130	0.1821	0.1597	0.0987
160	0.2492	0.2153	0.2553

Table 4. Activation energy at the initial (E_1) and final (E_2) stage of dehydration.

Samples	E_1 (kJ mol^{-1})	E_2 (kJ mol^{-1})	E_2/E_1
Batch I	13.04	15.69	1.203
Batch II	11.57	13.83	1.195
Batch III	16.53	21.82	1.320

Table 5. Values of reaction rate constant k_1 (min^{-1}), L_∞ (g), and extent of validity EV (%) of first order law for dehydroxylation of the gel at different temperatures.

Temperature (°C)	Batch I			Batch II			Batch III		
	k_1	L_∞	EV	k_1	L_∞	EV	k_1	L_∞	EV
350	0.0880	0.0610	65.29	0.0950	0.0509	69.06	0.0920	0.0520	62.37
380	0.1240	0.0825	68.30	0.1360	0.0614	72.11	0.1200	0.0697	64.27
410	0.2520	0.0886	70.06	0.2680	0.0688	75.66	0.2540	0.0821	68.05
440	0.2860	0.0912	74.30	0.2940	0.0792	78.58	0.2790	0.0922	71.26
470	0.3010	0.0949	76.27	0.3130	0.0825	80.20	0.3020	0.0979	73.47
500	0.3320	0.0996	79.09	0.3460	0.0871	83.08	0.3510	0.1006	75.88

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Table 6. Reaction rate constant (k_2 in min^{-1}) at the final stage of dehydroxylation.

Temperature (°C)	Batch I	Batch II	Batch III
350	0.114	0.080	0.078
380	0.120	0.127	0.119
410	0.232	0.241	0.237
440	0.269	0.272	0.271
470	0.288	0.298	0.289
500	0.320	0.320	0.328

Table 7. Activation energy at the initial (E_1) and final (E_2) stage of dehydroxylation.

Samples	E_1 (kJ mol^{-1})	E_2 (kJ mol^{-1})	E_2/E_1
Batch I	29.99	33.74	1.125
Batch II	28.12	32.36	1.151
Batch III	46.28	63.28	1.367

5. Conclusions

1. The mixed hydroxide hydrogel of MgO–ZrO$_2$ system contained two types of water viz., loosely bound gel water expelled at low temperature and constitutional hydroxyl water requiring higher temperature for expulsion. The dehydration reaction is heterogeneous in nature and is mostly controlled by the diffusion process.

2. The kinetics of the dehydration process followed 1st order law for both types of water and the Guggenheim equation can be applied for determining the kinetic parameters. The dehydration reaction in either case did not follow a single path and 1st order kinetics was valid up to a certain extent depending on the composition and temperature.

3. The reaction rate constants both at the initial and final stages of reaction exhibited true characteristics of endothermic reaction and the magnitudes were composition dependent.

4. Activation energy at the initial stage was always lower than that at the final stage of dehydration. Expulsion of hydroxyl water was comparatively a high energy process.

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