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Role of some transition metal cations on the kinetics of thermal dehydration of synthetic zeolites

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Abstract

Zeolite was synthesized by the interaction of sodium silicate and sodium aluminate solution. The gel formed was purified and physico-chemically characterized. The gel was converted into different cationic forms, like, Ni^{2+}, Co^{2+}, Cd^{2+}, etc., by ion exchange process. Isothermal dehydration kinetics of the hydrogel was studied from thermo-gravimetry. The gel dehydration reaction was observed to be low energy diffusion controlled process and the major part of the process followed first order kinetics. Exchangeable cations affected the kinetic parameters of the dehydration process.

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Keywords: Hydrogel; Zeolite; Transition metal cations; Isothermal kinetics

1. Introduction

Zeolites are hydrated aluminosilicates. The synthetic zeolites have certain advantages over naturally occurring zeolites in terms of occurrence, homogeneity and ion exchange capacity. In zeolite lattice structure some of the Si^{4+} ions are replaced by Al^{3+} ions. The charge deficiency is compensated by the exchangeable alkali or alkaline earth cations. Due to the complexity and the diversity in its structures and applications, many researchers have worked on the synthesis, characterization and application of zeolite [1–8].

In the present investigation sodium aluminosilicate hydrogel, popularly known as synthetic zeolite was synthesized by the interaction of sodium silicate and sodium aluminate solution under ambient temperature for an equilibrium period. Water is an integral part of the zeolite structure and it controls many of its important properties. Therefore, kinetics of the isothermal dehydration of synthetic sodium aluminosilicate hydrogel was studied with respect to the variation in exchangeable cations. The kinetics of this dehydration belongs to heterogeneous solid-state reaction and the basis for the understanding of the rate process was Arrhenius relationship. The relative influence of the exchangeable cations was compared by determining the rate constants and activation energies of the dehydration process for these samples.

2. Experimental

Sodium aluminosilicate hydrogel was synthesized by the wet interaction of sodium silicate and sodium aluminate solutions. The chemical composition of the starting materials, i.e., sodium aluminate and sodium silicate is given in Table 1. The molar ratio of Al_2O_3 and SiO_2 was kept fixed at 1:4 in the reacting solutions. The required proportions of silicate and aluminate solutions were taken separately and both were diluted to 3% solid content. Then diluted sodium aluminate solution was added to sodium silicate solution and mixed thoroughly for 1 h at ambient temperature. The mixed solutions was converted into a gel mass and it was allowed to age for 48 h. The gel was dispersed in large volume of de-ionized water and the supernatant liquid was siphoned off to remove the soluble impurities. The process was repeated for several times to get the maximum purity of the gel. Afterwards the gel was filtered and washed with distilled water. The washed mass was dried and ground to $-20+50$ mesh. The dried gel was chemically analyzed and the result is given in Table 2. IR analysis of the

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Table 1
Physico-chemical characteristics of the synthetic sodium alumino silicate gel

Chemical analysis (%)	Empirical formula	Bulk density (g/cm^3)	True density (g/cm^3)	DTGA peak temperature (°C)	Amount of transition metals incorporated (%)
SiO_2: 45.22 Al_2O_3: 5.63 Na_2O: 15.58 H_2O: 13.57	Na_2O, Al_2O_3, $3SiO_2$, $3H_2O$	0.485	2.10	220	NiO: 16.42 ZnO: 17.63 CuO: 17.30 CoO: 16.54 CdO: 23.25

dried gel samples was carried out with a Hitachi spectrophotometer (270-30). The gel was converted into different cationic forms by batch-wise ion exchange technique. Chloride salts (0.5 M) of five different cations (Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+}) were prepared for this purpose. The gel powders were mixed with excess of the salt solution at room temperature for a period of 24 h to carry out the ion exchange reaction. The ion exchanged gel powders were filtered, washed and dried. Kinetics of isothermal dehydration of the different zeolite samples were carried out with a thermo-gravimetric apparatus.

3. Results and discussion

From the chemical analysis of the hydrogel sample it was observed that the molar ratio of Na_2O:$A1_2O_3$ was1:1. It indicated the existence of aluminosilicate framework where all Al atoms had substituted Si atoms in the framework. The appearance of a single DTGA peak at 220 °C indicated the presence of a single silicate hydrate in the product. Some specific bonding to the channel of the aluminosilicate lattice associated the hydrate. Bulk density of the gel was significantly low (0.485 g/cm^3) due to the presence of pores and channels in the grains.

Table 2
Reaction rate constants (K_1) and L_α values as calculated from log ΔL vs. time plot of the different zeolites at different temperatures

Name of the zeolite	Temperature (°C)	K_1 (min^{-1})	L_α (g)
Ni–zeolite	130	0.1595	0.0286
	160	0.2355	0.0311
	190	0.2971	0.0366
	220	0.3861	0.0381
	250	0.4606	0.0425
	280	0.5137	0.0502
Zn–zeolite	130	0.2038	0.0211
	160	0.2456	0.0290
	190	0.2798	0.0321
	220	0.3859	0.0383
	250	0.4459	0.0457
	280	0.4844	0.0535
Cu–zeolite	130	0.1902	0.0220
	160	0.2752	0.0298
	190	0.3102	0.3170
	220	0.4044	0.0364
	250	0.4441	0.0453
	280	0.4670	0.0529
Co–zeolite	130	0.1924	0.0223
	160	0.2251	0.0303
	190	0.3140	0.0383
	220	0.3377	0.0370
	250	0.3874	0.0484
	280	0.4277	0.0494
Cd–zeolite	130	0.2060	0.0183
	160	0.2873	0.0242
	190	0.3644	0.0246
	220	0.4121	0.0286
	250	0.4513	0.0385
	280	0.4730	0.0481

Except Zn^{2+} and Cd^{2+} all the other cationic forms of the gels exhibited colour. During conversion to the different cationic forms, no decomposition or size reduction of the gel sample occurred. From an analysis of the cation exchange in the reverse process it was found that about 90% of the theoretical exchange took place in the samples.

Water is an integral part of the zeolite structure and the dehydration behavior of the zeolites definitely depends on the bonding nature of the water present in the structure. It is influenced by the presence of the exchangeable cations in the samples. In the IR spectra of the samples –OH stretching and bending vibrations was observed in all the cases but the intensity of the vibrations varied in the samples. This vibration is a function of the cationic force field acting on the water molecules, which varied due to the variation in the ionic potential of the substituted cations (Figs. 1 and 2).

From the DTGA diagram of all the cationic form of the gels (Fig. 3) it was observed that the major part of the dehydration in all the samples took place in the temperature range 220 °C and the magnitude of dehydration varied from sample to sample. The initial plots of the weight loss against time followed exponential behavior in the isothermal dehydration loss

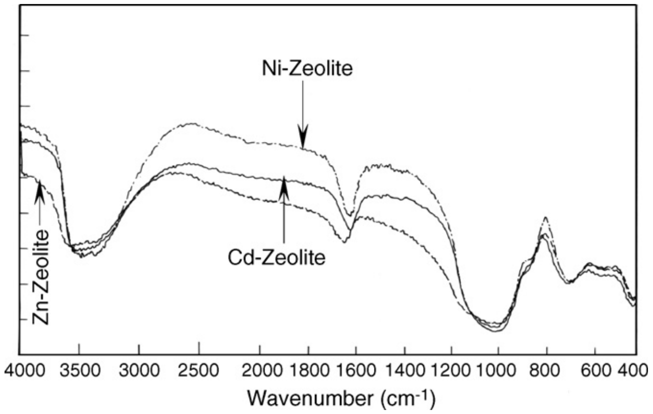

Fig. 1. IR spectra of the aluminosilicate hydrogel with Zn^{2+}, Cd^{2+} and Ni^{2+} as exchangeable cations.

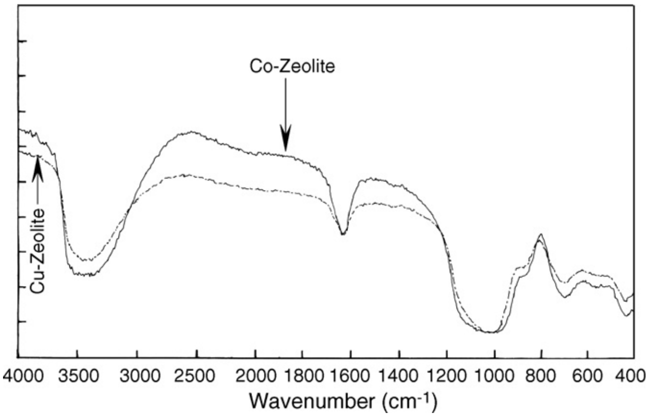

Fig. 2. IR spectra of the aluminosilicate hydrogel with Cu^{2+} and Co^{2+} as exchangeable cations.

measurements of the powder samples. Therefore, the application of first order kinetics appeared to be logical where the weight loss of water from the sample at any instant would be proportional to the concentration of the water present in the sample at that instant. Now, the concentration of water present in the sample would be equal to the weight of water present in it, which can be lost at the experimental temperature, divided by the volume of the sample. Therefore, if the weight and hence the volume of the initial sample is kept fixed, the concentration term may be replaced by the relevant weights. Thus at a given temperature if:

- L: weight loss at time t;
- L_α: total weight loss at infinite time.

Then L_α is equivalent to the initial concentration of water dehydratable at the experimental temperature in the sample and $(L_\alpha - L)$ 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

$$\frac{dL}{dt} = K(L_\alpha - L) \quad \text{or} \quad \log\frac{L_\alpha - L}{L_\alpha} = -\frac{Kt}{2.303} \tag{1}$$

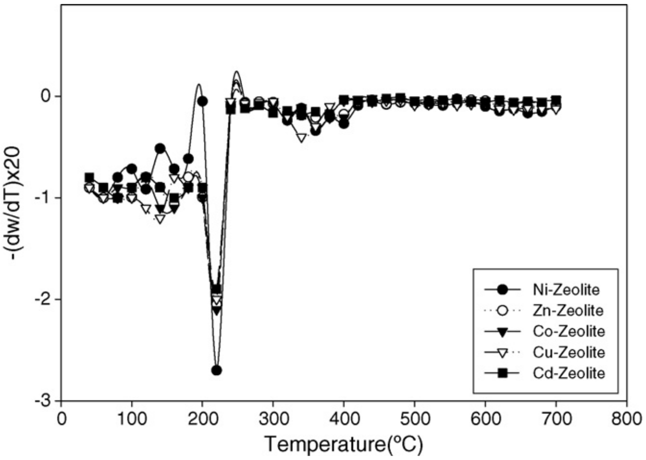

Fig. 3. DTGA diagram of the different cationic form of zeolites.

Eq. (1) permits evaluation of the rate constant for dehydration (K) from the slope of the line obtained by plotting log $[(L_\alpha - L)/L_\alpha]$ against 't' provided we know the value of L_α. As the first order reaction can never go to completion theoretically, any direct determination of L_α would be inaccurate and was not at attempted. Instead, the method originally suggested by Guggenheim and followed by Mitra et al. [9] was adopted for evaluation of both L_α and K.

Let us suppose $L_1, L_2, \ldots, L_n$ be the weight losses at time $t_1, t_2, \ldots, t_n$ and let us suppose $L'_1, L'_2, \ldots, L'_n$ be the losses at time $(t_1 + \Delta t)$, $(t_2 + \Delta t)$, …, $(t_n + \Delta t)$, the set of readings L' was taken at constant time interval "t" after the previous set L. Using Eq. (1) we can write:

$$L_\alpha - L_1 = L_\alpha \exp(-K_1 t_1) \quad \text{and}$$

$$L_\alpha - L'_1 = L_\alpha \exp[-k_1(t_1 + \Delta t)]$$

Subtracting:

$$L'_1 - L_1 = [L_\alpha \exp(-k_1 t_1)][1 - \exp(-k_1\, \Delta t)]$$

Taking logarithms and putting ΔL for $(L' - L)$ the equation takes the general form:

$$\log \Delta L = \left(\frac{-K_1 t}{2.303}\right) + \log[L\alpha(1 - \exp(K_1 \Delta t)] \tag{2}$$

In the above equation ΔL is the difference in between the weight loss at time $t + \Delta t$ and at time t, the time interval Δt between the two sets of readings being kept fixed at values greater than twice the time for 50% dehydration. Using Eq. (2) the rate constants can be calculated from the slope of the straight line

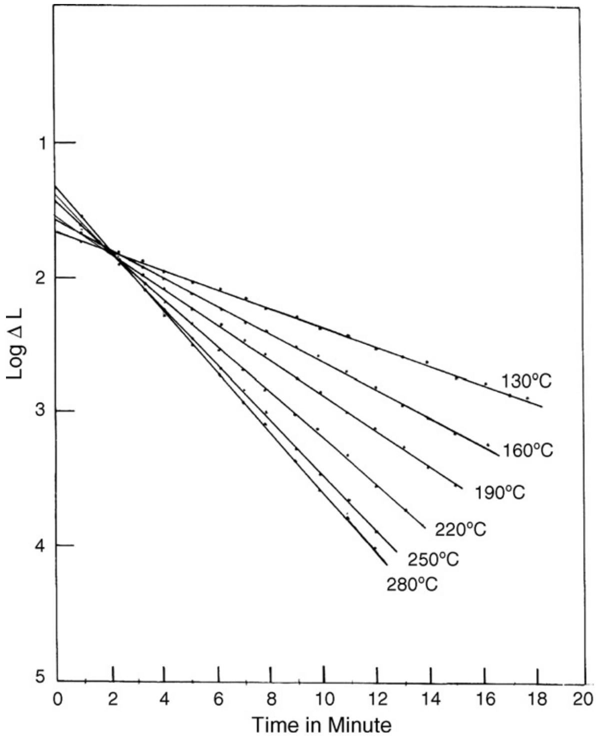

Fig. 4. Plot of log ΔL vs. time for the isothermal dehydration of Ni–zeolite at different temperatures.

Table 3
Extent of validity of first order law as determined from the $\log(L_\alpha - L)/L_\alpha$ vs. time plot during dehydration of zeolites at the initial stage

Name of the zeolite	Percentage validity of first order at different temperatures (°C)					
	130	160	190	220	250	280
Ni–zeolite	71.32	74.32	76.78	79	80.47	83.26
Zn–zeolite	70.14	73.79	76.63	80.41	83.15	85.6
Cu–zeolite	68.18	71.18	73.13	76.64	79.91	82.79
Co–zeolite	72.64	74.58	77.27	80	82.23	84.21
Cd–zeolite	69.39	71.9	75.2	79.02	80.77	83.16

obtained by plotting $\log \Delta L$ against 't'. Knowing Δt, and having obtained K_1 from the slope, we can determine L_α from the intercept by the line on the $\log \Delta L$ axis.

The rate constants and L_α values were determined from the plots of $\log \Delta L$ versus t (Fig. 4) and these are given in Table 3. Variation of reaction rate constant with change of exchangeable cation was not remarkable. At 280 °C maximum rate was observed with Ni–zeolite and minimum rate was observed with Co–zeolite. True endothermic nature of the reaction was reflected through the temperature effect.

In each cationic form of the hydrogel L_α value was found to increase with temperature and the sequence of the cations with respect to L_α values at 280 °C can be given as

$$Zn^{2+} > Cu^{2+} > Ni^{2+} > Co^{2+} > Cd^{2+}$$

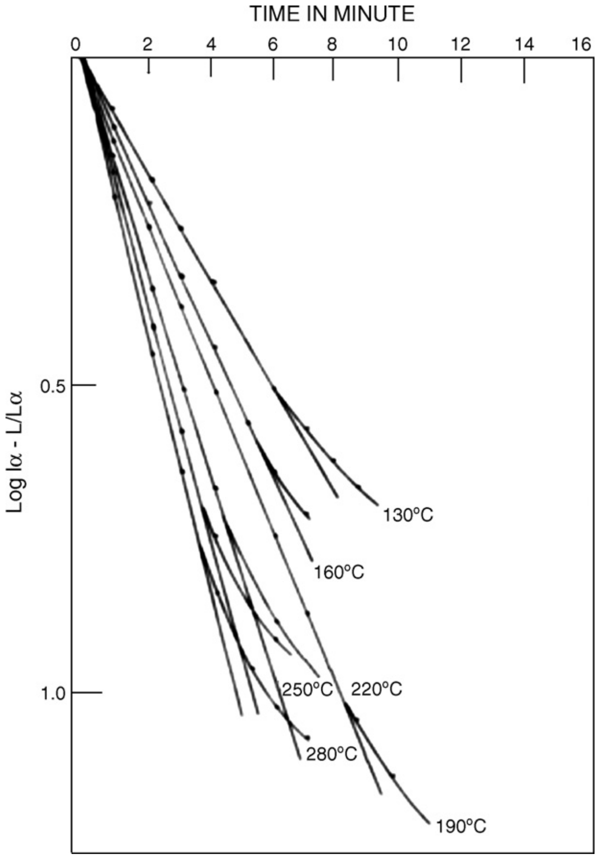

Fig. 5. Plot of $\log(L_\alpha - L)/L_\alpha$ vs. time for the isothermal dehydration of Ni–zeolite at different temperatures.

Table 4
Values of reaction rate constant of zeolites at different temperatures

Name of the zeolite	K_2 value (min^{-1}) of different zeolites (°C)					
	130	160	190	220	250	280
Ni–zeolite	0.1792	0.1874	0.2135	0.2988	0.3890	0.5027
Zn–zeolite	0.2644	0.2819	0.3110	0.3554	0.4870	0.5194
Cu–zeolite	0.2380	0.3027	0.3150	0.3641	0.4478	0.5086
Co–zeolite	0.2321	0.2791	0.3324	0.3542	0.3875	0.4962
Cd–zeolite	0.2167	0.3195	0.3684	0.3878	0.4500	0.4783

The difference in L_α values was mainly due to the variation of cationic nature. The variation was within a very narrow range. The whole course of the dehydration reaction was not uniform and as such it was necessary to find out how far the first order law was valid for the experimental sample. For this purpose L_α values as determined earlier, were used for the construction of $\log(L_\alpha - L)/L_\alpha$ versus time plots. Such plots (Fig. 5) showed positive deviation from linearity after a certain range and from this deviation, limits of applicability of the first order kinetics have been determined which are given in Table 4.

From the above results it may be concluded that the extent of validity of the first order kinetics followed a linear relationship with temperature. About 85% of the total dehydration reaction followed first order kinetics. Variation of this validity among the different cationic from of the hydrogel was not of high order still the maximum variation was observed with Zn^{2+} containing hydrogel. This might be due to textural factors of the gels during the heat treatment.

When the weight loss of the gel samples was plotted against the dehydration time, a parabolic rate curve was obtained for all the samples (Fig. 6). It suggested that the dehydration reaction

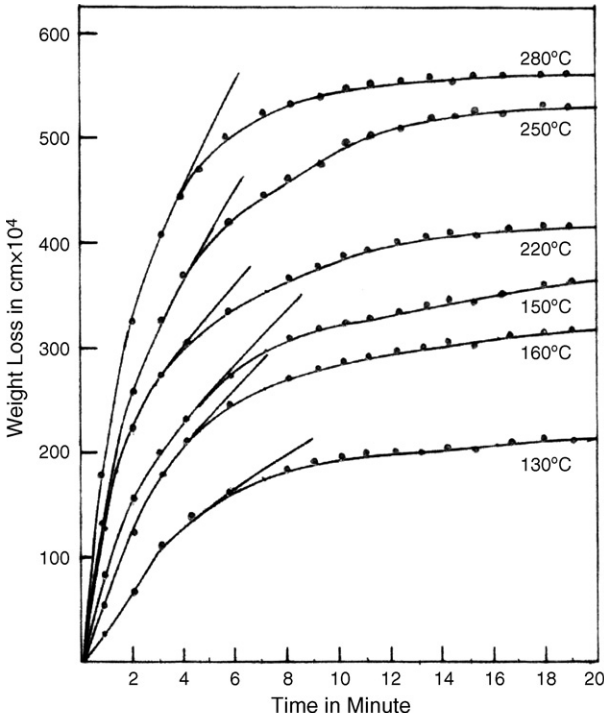

Fig. 6. Plot of weight loss vs. time of Ni–zeolite at different temperatures.

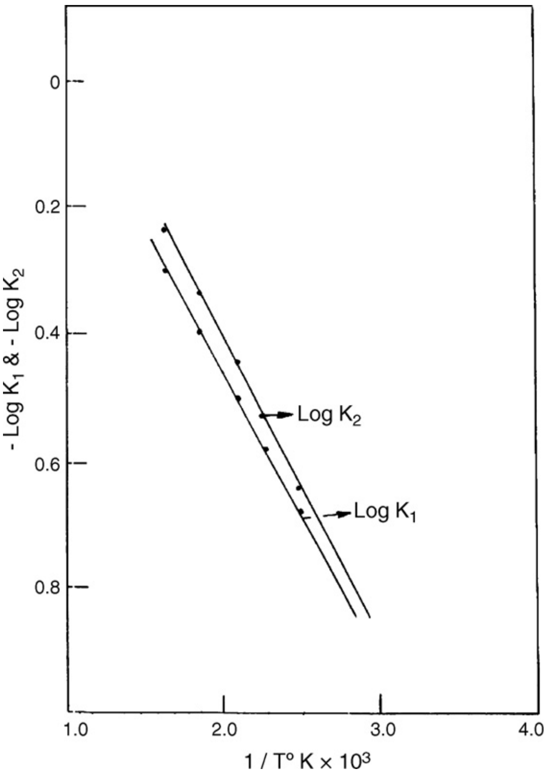

Fig. 7. Arrhenius plot for the initial and final stage of dehydration for Ni–zeolite.

in amorphous aluminosilicate hydrogel is purely diffusion controlled heterogeneous solid-state reaction. During the heat treatment process water molecule is formed in the structure and the formed water molecules diffused through the aluminosilicate network for evaporation. The dehydration rate depends on the diffusion rate of the water molecules through the structures. During the early stage of the dehydration reaction recombination process (of the dislodged water molecules) due to the cooling effect interfered with the course of the reaction and it resulted in the deviation from the first order law.

However, it is evident that the last portion of water was lost at a rate, which was completely different from that prevailing at the earlier stage. It was reflected through the flattening of the rate curves. The dehydration rate at latter stages would still proportional to the concentration of the remaining water.

Thus, it is clear from the breaks in linearity that the dehydration process by thermal treatment can be subdivided into two stages. The rate constants K_2 for the latter stage of dehydration were calculated from the relation.

$$K_2 = \frac{\mathrm{d}L/\mathrm{d}t}{L_\alpha - L} \tag{3}$$

where dL/dt is the slope of the weight loss versus time curve at the point of dehydration beyond which first order kinetics was not followed:

- L: actual loss at the point;
- L_α: total equilibrium loss at the experimental temperature.

Table 5
Activation energies from Arrhenius plot of different zeolites during dehydration

Name of the zeolites	Activation energy (kcal/mol)	
	Initial stage (E_1)	Final Stage (E_2)
Ni–zeolite	2.646	3.008
Zn–zeolite	2.543	2.846
Cu–zeolite	2.264	2.313
Co–zeolite	2.094	2.178
Cd–zeolite	2.661	2.783

Calculated values of K_2 for the final stage of dehydration are given in Table 5. K_2 values were not identical to K_1 values and the variation with temperature did not exhibit any anomalous behavior.

Activation energy is actually the height of the energy barrier to the dehydration reaction and it was calculated from the slope of the curves (Fig. 7) in accordance with the Arrhenius equation:

$$\log K = \log(PZ) = \frac{E}{4.576T} \tag{4}$$

The calculated values of activities energies for the initial and final stages of dehydration, i.e. E_1 and E_2 are given in Table 5.

E_1 and E_2 values were related to the nature of bonding of water molecules to the gel structure. In the present investigation the nature of the exchangeable cation was the variable parameter. In each case E_2 values were higher than the corresponding E_1, values indicating dependence of the dehydration reaction on the concentration of the reacting species. The gel network is extremely porous and always is in strained condition. Thus, during expulsion of water molecules at the earlier stage of dehydration although the lattice suffered shrinkage but at the same time some flaws were also created which enhanced the diffusion rate of water molecules at the final stage of dehydration. This was evident from the results that the difference between E_2 and E_1 values was very small. The ratio E_2/E_1 was slightly higher than 1 and it was the maximum with Zn^{2+} and the minimum with Cu^{2+} form of the hydrogel.

4. Summary and conclusion

Sodium aluminium silicate hydrogel with Al_2O_3:SiO_2 molar ratio of 1:3 was synthesized by the interaction of sodium silicate and synthesized sodium aluminate. The gel was converted into different transition metal cations, like Cu^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+} forms by ion exchange. From the IR spectra of the dried gel it was observed that the orientation of the water molecules in these different cationic forms of hydrogel was different. The dehydration process was observed to be diffusion controlled and the major portion of the reaction in each case followed first order kinetics. The activation energies of the process were observed to be quite low and the transition metal cations affected the percent validity of the first order kinetics and the activation energies of the dehydration process depending.

References

[1] G. Giannetto, L. García, J. Papa, F. Yánez, M.R. Goldwasser, C. Linares, D. Moronta, B. Mendez, C. Urbina de Navarro, R. Monque, Synthesis and characterization of [Cr,Al]-ZSM-5 zeolites, Zeolites 19 (1997) 169–174.

[2] D. Akolekar, A. Chaffe, R.F. Howe, The transformation of kaolin to low silica × zeolite, Zeolites 19 (1997) 359–365.

[3] Z. Lai, M. Tsapatsis, J.P. Nicolich, Siliceous ZSM-5 membranes by secondary growth of b-oriented seed layers, Adv. Funct. Mater. 14 (2004) 716–729.

[4] F.S. Xiao, S. Qui, W. Pang, R. Xu, New developments in microporous materials, Adv. Mater. 11 (1999) 1091–1999.

[5] Y. Wang, F. Caruso, Microporous zeolite membrane bioreactors, Adv. Funct. Mater. 14 (2004) 1012–1018.

[6] T. Nanb, Y. Suzuki, Membrane-like synthetic zeolites, Jpn. Kokai Tokkyo Koho 95,247,115, September 26, 1995; Appl. March 15, 1994.

[7] R.J. Saxton, J.G. Zaiacek, Preparation of an aluminosilicotitanate isomorphous with zeolite, p. U.S. 5,474,754, December 12, 1995; Appl. August 15, 1994.

[8] R. Kuroda, J. Arima, K. Takakura, Manufacture of faujasite-type zeolites by aging, Jpn. Kokai Tokkyo Koho 95,232,914, September 5, 1995; Appl. February 17, 1994.

[9] N.K. Mitra, K.L. Roy, S. Mitra, Kinetics of thermal dehydration of synthetic sodium aluminosilicate hydrogel, Trans. Br. Ceram. Soc. 74 (1975) 263–265.