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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.

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.

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

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

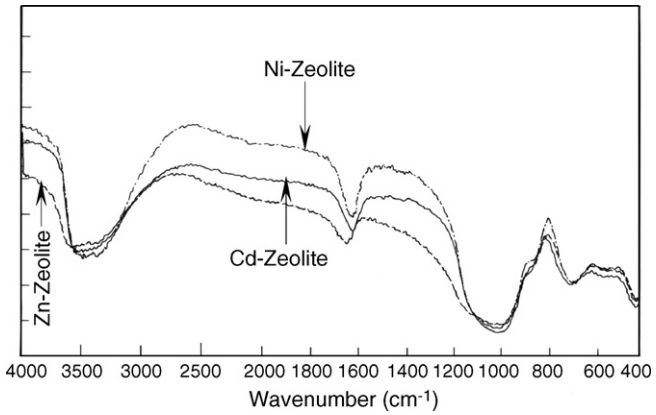

Fig. 1. IR spectra of the aluminosilicate hydrogel with Zn^{2+}, Cd^{2+} and Ni^{2+} as exchangeable cations.