

TG AND DTA STUDY OF THE THERMAL DEHYDRATION OF METAL-EXCHANGED ZEOLITE-4A SAMPLES

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Abstract

Zeolite-4A is a hydrated aluminosilicate which becomes more hydrated when exchanged with transition metals. In this work, the dehydration kinetics of cobalt, nickel and copper(II)-exchanged zeolite-4A were studied by means of TG and DTA over the temperature range from 20 to 500°C, and the numbers of water molecules in the metal-exchanged zeolite samples were calculated. It was observed that, as the ionic radius of the hydrated metal increased, the number of water molecules also increased. The loss of water from the zeolite samples generally occurred in the temperature range 100–300°C and was manifested in the DTA graphs by an extended endothermic effect. The DTA curves demonstrated that the peak position shifted towards lower temperatures as the metal concentration increased or, in other words, the water of hydration increased. The kinetic parameters (order of reaction and activation energy) were calculated via the Coats and Redfern method. The process of dehydration was found to follow first-order kinetics.

Keywords: kinetics, metal exchange, thermal dehydration, zeolite

Introduction

The dehydration forms of synthetic zeolites are of use in selective absorption and catalysis, in consequence of the presence of interconnecting channels and cavities of definite shape and uniform size [1]. The characteristic properties of zeolites, such as their acidity, shape selectivity and thermal stability, are also suitable for their use for highly selective syntheses in the fields of chemical intermediates and fine chemicals [2, 3]. The water molecules in the aluminosilicate framework act as guests that can be out-gassed continuously over a wide temperature range by heating in air, leaving an empty porous structure, which can be filled by other suitable molecules. The dehydrated zeolites are known as ‘molecular sieves’, due to their property of permitting only molecules of definite size and shape to enter the empty cavities, depending on

their channel sizes, which are distributed uniformly throughout the crystalline aluminosilicate network [4, 5].

A simple way to modify the stability, adsorption behaviour, selectivity, catalytic activity and other properties of zeolites is by cation exchange. The high thermal stability of the zeolite framework depends largely on the type of cation, its distribution among the non-framework sites, and the degree of cation exchange. Cation exchange with multivalent cations or the hydrogen ion enhances the thermal stability [6]. Few data are available on the dehydration of metal-exchanged zeolites [7–10]. Our results are comparable with those of Gal *et al.* [10]. The dehydration kinetics of pure zeolites, and the thermal decomposition of metal acetates and metal-doped carbons have been studied in this laboratory [11–16].

Experimental

The zeolite-4A was supplied by Merck. It was ground in an agate mortar and passed through U.S. standard sieve series No. 140 having an opening of 105 microns. The metal(II) chlorides used were supplied with a purity better than 99% by Merck.

Metal-exchanged samples were prepared by magnetically stirring a predetermined amount of metal chloride and zeolite-4A in 100 ml of distilled water at different temperatures for different time intervals. The amount of metal exchanged was determined by an EDTA microtitration method. The metal-exchanged zeolite samples are designated by the formula M_xX , where M stands for Co, Ni or Cu, x is the number of metal ions per unit cell and X is the residue.

The effects of temperature on these samples were studied by using a Shimadzu Thermal Analyzer (TG-31). A known mass of sample was placed in a crucible and suspended in a quartz tube; it was possible to control the atmospheric gases inside the system. The sample was heated at a rate of $10^\circ\text{C min}^{-1}$ to a temperature of 500°C under a constant flow of air. The changes in the mass of the sample with elevation of temperature were recorded by a photocell. The output of the photocell was amplified and measured continuously and precisely by recording the current through an automatic recorder model R-22T.

For DTA measurements, weighed amounts of the sample and of the reference substance (inert alumina) were placed in two separate cells and transferred onto the dumbbell-type detector. The sample and reference material were then heated together, at a rate of $10^\circ\text{C min}^{-1}$ under a constant flow of air. When a thermal reaction occurred in the sample in response to heating, a difference in temperature resulted between the sample and the standard sample. This difference was detected by the dumbbell-type detector, amplified by the direct current amplifier, and recorded as a DTA curve.

Results and discussion

The TG and DTA curves of all the samples revealed an endothermic mass loss due to dehydration (Figs 1–6). The mass loss was initiated at 50 and was almost complete at

400°C for both pure and metal-exchanged zeolites. A difference was observed in the temperature range mentioned above, where the mass loss for the metal-exchanged zeolite was greater than that for the pure zeolite, which means that, with increasing metal concentration, the mass loss increased, besides the number of water molecules. The DTA maximum peak for the pure zeolite was observed at 125°C, while for the metal-exchanged zeolite (except for $\text{Cu}_{5,0}\text{A}$) the main peak was shifted towards lower temperature by about 10–20°C. This means that the transition metal ions increase the DTA peak intensity and shift the peak position towards lower temperature.

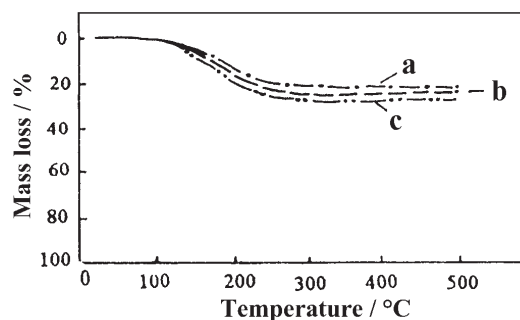


Fig. 1 TG curves for a – NaA-zeolite; b – $\text{Co}_{3,73}\text{A}$; c – $\text{Co}_{5,27}\text{A}$

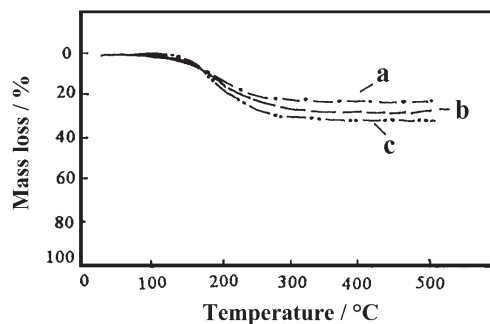


Fig. 2 TG curves for a – NaA-zeolite; b – $\text{Ni}_{2,54}\text{A}$; c – $\text{Ni}_{3,61}\text{A}$

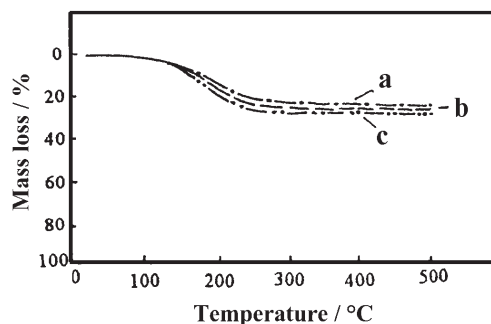


Fig. 3 TG curves for a – NaA-zeolite; b – $\text{Cu}_{3,64}\text{A}$; c – $\text{Cu}_{5,0}\text{A}$

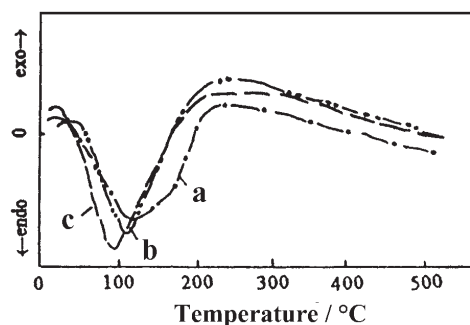


Fig. 4 DTA curves for a – NaA-zeolite; b – Co_{3.73}A; c – Co_{5.27}A

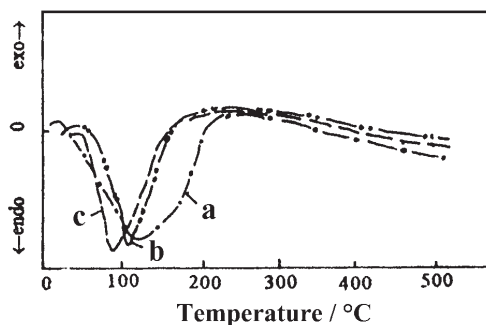


Fig. 5 DTA curves for a – NaA-zeolite; b – Ni_{2.54}A; c – Ni_{3.61}A

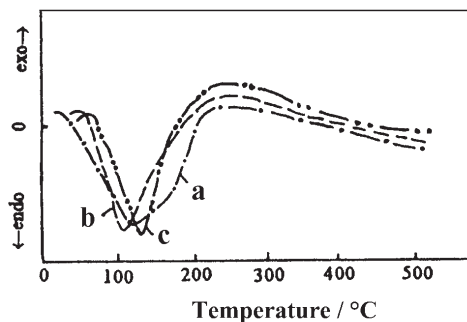


Fig. 6 DTA curves for a – NaA-zeolite; b – Cu_{3.64}A; c – Cu_{5.0}A

It was observed that, as the metal concentration was increased, the water content also increased. It has been reported by Breck [17] that the presence of different cations in the zeolite-A voids affects the pore volume. A small divalent cation increases the void volume by reducing the total number of cations and increasing the space unoccupied. According to the valence rule, 2 Na⁺ are exchanged by 1 M²⁺; moreover, the Pauling ionic radii for Co²⁺ and Na⁺ are 0.74 and 0.95 Å, respectively [18], and the empty space in the cavities therefore increases when Na⁺ is replaced by Co²⁺. Hence, an increased number of water molecules is to be expected in the zeolite in consequence of Co(II) exchange. In

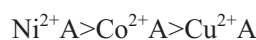
general, the number of water molecules lost per unit cell increases with increasing concentration of Co^{2+} in the zeolite. This indicates that, in the NaA-zeolite, which contains no complex-forming cations, the water molecules just fill the cavities and channels, and can easily be removed by outgassing in vacuum. The water molecules do affect the specific positions of exchangeable cations in these zeolites, but they do not appear to have any primary structural function and can be removed reversibly without disrupting the framework structure; when hydrated, the zeolite can be regarded as a polyanionic framework surrounded by a solution of positive ions in water. In the synthetic zeolite of type A, this interstitial solution of Na^+ contain 24 moles of Na^+ per 1000 g of water. When suspended in water, the zeolite of type A produces hydroxide ions due to limited hydrolysis of the more loosely bound cations [17].

Table 1 demonstrates the increase in water content per unit cell of Ni(II)A-zeolite with increasing Ni^{2+} content per unit cell. The same reasons are suggested for the increased water content of Co^{2+} A-zeolites as for the Ni^{2+} A-zeolites. The Table shows that in general the number of water molecules per unit cell of Ni(II)A-zeolite is higher than that for Co(II)A-zeolite. According to Cotton and Wilkinson [18], the size of Ni^{2+} is smaller than that of Co^{2+} . This indicates a high degree of ordering of the water molecules around Ni^{2+} and hence a greater hydration ability of Ni^{2+} than that of Co^{2+} in hydrated zeolite-A. Dyer and Wilson [19] and Coughlan and Carrol [20] reported an increased water content per unit cell for a number of Ni(II)A-zeolites with increasing degree of exchange.

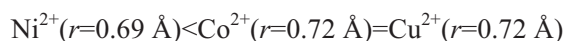
Table 1 Kinetics parameters for dehydration of metal-exchanged zeolites

System	DTA $T_{\text{max}}/^{\circ}\text{C}$	Mass loss/%	No. of water molecules	$E/\text{kJ mol}^{-1}$
NaA	125	22.2	27	15.35
$\text{Co}_{3.73}\text{A}$	112	24.8	30	13.51
$\text{Co}_{5.27}\text{A}$	90	26.3	33	12.55
$\text{Ni}_{2.54}\text{A}$	110	25.4	31	12.80
$\text{Ni}_{3.61}\text{A}$	88	27.1	34	11.71
$\text{Cu}_{3.64}\text{A}$	112	23.4	29	12.43
$\text{Cu}_{5.0}\text{A}$	128	24.2	30	10.04

In general, the numbers of water molecules obtained per unit cell for Co^{2+} , Ni^{2+} and Cu^{2+} -exchanged zeolite-A were in the following sequence:



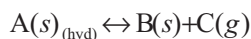
This sequence seems quite sensible, because the ionic radii [21] lie in the following sequence:



The above sequence of ionic radii shows that Co^{2+} and Cu^{2+} are equal in size, but Co^{2+} A-zeolite has a higher water content than that of Cu^{2+} A-zeolite; this might be due to the greater ordering of water molecules around Co^{2+} as compared with Cu^{2+} . The radius of the hydrated ion [22] for Na^+ is 3.58, that for Co^{2+} is 4.23, that for Ni^{2+} is

4.04, and that for Cu^{2+} is 4.19 Å, which supports the above discussion. For the metal-exchanged zeolites, therefore, it can be stated that, just as hydration is easy for transition metals as compared with sodium, so is dehydration. This is confirmed by the DTA curves and has also been shown by Gal *et al.* [10].

The process of dehydration of zeolites is reported [23–27] to be of the reaction type



and is usually described by the well-known kinetic equation.

$$\frac{d\alpha}{dt} = A_0 \exp\left(-\frac{E}{RT}\right) (1-\alpha)^n \quad (1)$$

where α is the reacted fraction of the crystallized phase at time t , n is the order of reaction, and A_0 is the pre-exponential factor.

The kinetic parameters for the above-mentioned samples were determined by employing the Coats and Redfern [27] method. For order $n=1$, the equation reaction reduces to

$$\log\left[\frac{-\log(1-\alpha)}{T^2}\right] = \text{constant} - \frac{E}{2.303 RT} \quad (2)$$

A plot of $\log[-\log(1-\alpha)/T^2]$ vs. $1/T$ is linear (Fig. 7), and the energy of activation is calculated from the slope.

A computer program was designed to evaluate the order of reaction and the energy of activation. The best straight line was obtained for the first-order rate equation and hence n was taken to be unity for all systems.

From the data, it can be concluded that the activation energies for the metal-exchanged samples are low as compared with that for the parent zeolite, because the transition metals are easy to dehydrate as compared with sodium, as mentioned above.

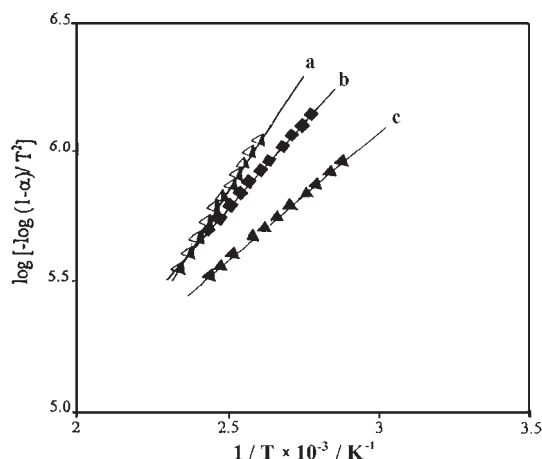


Fig. 7 Plots of $\log[-\log(1-\alpha)/T^2]$ vs. $1/T$ for a – NaA-zeolite; b – $\text{Co}_{3.73}\text{A}$; c – $\text{Co}_{5.27}\text{A}$

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