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KINETIC STUDY OF THE DEHYDRATION OF MODIFIED Y ZEOLITES *

S.J. KULKARNI ** and S.B. KULKARNI

Physical Chemistry Division, National Chemical Laboratory, Poona 411008 (India)

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ABSTRACT

The dehydration of ferric exchanged Y zeolites is studied by thermal analysis. Their DTA shows three endotherms in the temperature range 80–450°C. The order of reaction and apparent energies of activation are calculated using various equations. The order of dehydration is nearly one and the apparent energy of activation is 4–8 kcal mole^{-1}. The effect of heating rate is studied. The energy of activation as determined by the Kissinger and Ozawa method is about 12 kcal mole^{-1}, which is comparable with the heat of adsorption of water determined by the gravimetric method, and is more acceptable.

INTRODUCTION

The process of dehydration of zeolites, crystallohydrates, can be studied well by thermal analysis. Rassonskaya [1] has reported kinetic parameters for the dehydration of zeolites. He obtained an energy of activation for dehydration of 4–8 kcal mole^{-1} by the Piloyan–Novikova method. In the present work, we are reporting apparent energies of activation for the dehydration of ferric exchanged Y zeolites, calculated by different methods, and the effect of heating rate.

EXPERIMENTAL

Linde NaY Zeolite, binder free (SK-40 Lot No. 96805000) obtained from Union Carbide, U.S.A., was used as the starting material for catalyst preparation. The ferric exchanged zeolites were prepared by treating Linde NaY Zeolite with aqueous solutions of ferric acetate–acetic acid at about pH 4 at 27–30°C with constant stirring. The X-ray diffractograms confirmed the crystallinity of the samples. All thermograms were recorded under identical conditions on an automatic Hungarian derivatograph (Model MOM-102) described by Paulik et al. [2]. The weight of the sample was 300 mg. Pre-heated and finely powdered α-alumina was used as a

* N.C.L. Communication No. 2861.

** To whom correspondence should be addressed.

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reference material. The heating rates were varied from 2–10°C min^{-1}. The DTA sensitivity was the maximum (1/1).

RESULTS AND DISCUSSION

Figure 1 shows typical thermograms for NaY and FeNaY (61) samples. The NaY zeolite shows a single endothermic peak corresponding to the dehydration in the temperature range 80–360°C. The exothermic peak corresponding to the structure breakdown of NaY is at 842°C. On the other hand, the DTA curves for ferric exchanged Y zeolites show three endotherms in the range 80–450°C and an exothermic peak at 840–870°C. The detailed analysis is given elsewhere [3,4].

The following equations are used to determine the apparent energies of activation for dehydration corresponding to the first endotherm at about 160°C of zeolite samples.

(1) Coats–Redfern equation [5]

$$\log\left[\frac{-\ln(1-\alpha)}{T^2}\right] = \log\frac{AR}{aE}\left[1-\frac{2RT}{E}\right] - \frac{E}{2.303\,RT}$$

where α = fraction dehydrated, a = heating rate, T = absolute temperature, R = gas constant, E = apparent activation energy.

(2) Kissinger equation [6]

$$n = 1.26\,(s)^{1/2}$$

where n = apparent order of reaction, s = shape index factor as defined by Kissinger [6].

$$\frac{\mathrm{d}\left(\ln\frac{a}{T_m^2}\right)}{\mathrm{d}\left(\frac{1}{T_m}\right)} = \frac{-E}{R}$$

where T_m = peak temperature, a = heating rate, °C min^{-1}.

(3) Ozawa equation [7]

$$\log a + 0.4567\,\frac{E}{RT_m} = \text{constant}$$

(4) Horowitz and Metzger equation [8]

$$\ln\ln(1-\alpha)^{-1} = \frac{E}{RT^2}(T_m - T)$$

(5) Modified Coats–Redfern equation [9]

$$\ln\left[\frac{1-(1-\alpha_1)^{1-n}}{1-(1-\alpha_2)^{1-n}}\left(\frac{T_2}{T_1}\right)^2\right] = \frac{E}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$$

The values of order of dehydration and apparent energies of activation are given

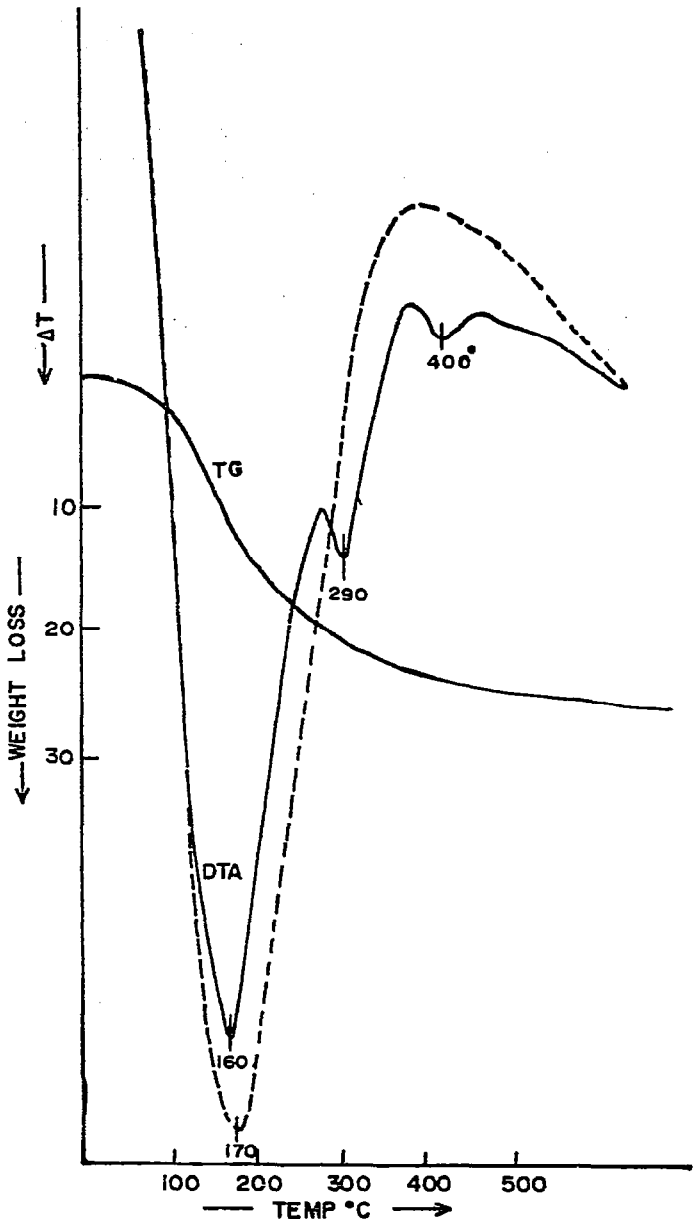

Fig. 1. Thermogram of FeNaY(61) and NaY.

in Table 1. The order of reaction was calculated by Kissinger's method [6].

The order of dehydration of zeolites was found to be nearly one. We have also calculated the order of dehydration by Balarin's method [10] but could not get consistent values, as they vary from 1 to 1.7. The apparent activation energy E, for dehydration is 4–6 kcal mole^{-1} for different samples, calculated by the Coats–Redfern method. A typical Coats–Redfern plot for FeNaY(61) is shown in Fig. 2. The energy of activation, E, calculated by the Horowitz and Metzger method is about 7 kcal mole^{-1}. However, the Piloyan–Novikova equation [11] was not applicable.

TABLE 1

Kinetic parameters for the dehydration of zeolites

Zeolite	Order of reaction Kissinger method			Energy of activation (kcal mole^{-1})i		Rate constant, k (arbitrary units)
	First endotherm	Second endotherm	Third endotherm	Coats–Redfern method	Horowitz–Metzger method	
NaY	1.23			5.58	7.18	0.97
FeNaY(37) *	0.99			5.46	7.00	0.92
FeNaY(44)	1.18	1.13	1.40	5.98	7.65	1.68
FeNaY(61)	1.26	0.99	1.26	5.32	7.45	1.98
FeNaY(75)	1.17	1.26	1.61	5.86	7.00	1.97
FeNaY(82)	1.18	1.02	1.03	4.23	7.45	1.78

* Bracketed number indicates the percent exchange. Heating rate was 5.3°C min^{-1}.

The values of rate constant are calculated by using the equation

$$k = \left(\frac{\Delta T}{A'}\right) / (1-\alpha)^n$$

where ΔT = the DTA peak height and A' = the area under the curve. The rate of dehydration for the first endotherm increases with the increase of ferric exchange as given in Table 1. The presence of aquocomplexes of ferric ions in supercages [4]

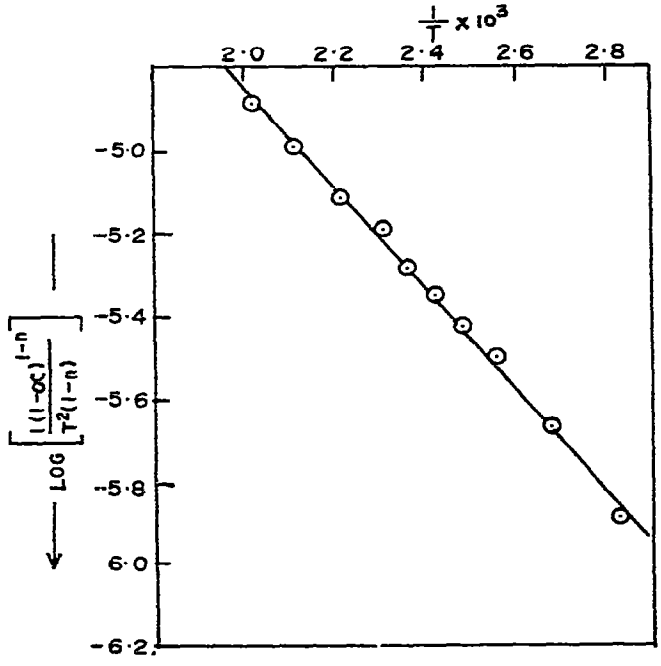

Fig. 2. Coats–Redfern plot of FeNaY(61).

hinders the physically adsorbed molecules making them comparatively less stable in supercages thereby increasing the rate of desorption of physically adsorbed molecules with the increase in the number of aquocomplexes of iron.

Effect of heating rate

It has been observed that the shapes of TG and DTA curves vary with a number of experimental parameters, such as heating rate, particle size, sample weight, furnace atmosphere, etc. [12]. The DTA peak temperatures at different heating rates for FeNaY(82) are given in Table 2. At lower heating rates (2.5 and 4.1°C min^{-1}), the first dehydration peak splits into two with minima at 90–100 and 170–190°C. For heating rates 2.5 and 4.1°C min^{-1}, the dehydroxylation endotherm at 400°C is absent. At higher heating rates, 8 and 10°C min^{-1}, the endotherm at ~90°C was not observed indicating its merging in the major endotherm at about 160°C. With an increase in the heating rate, the peak positions in the DTA curves were shifted towards higher temperatures, particularly in the case of the second and third endotherms. These changes may be due to incomplete equilibrium conditions in the non-isothermal dehydration of zeolites and obviously, the effect of the heating rate. Each endotherm indicates a type of water molecule with a different chemical environment. The DTA data support the multistep desorption of water which is a consequence of energetic heterogeneity of surface potential.

The values of the apparent activation energy of dehydration corresponding to the first endotherm for FeNaY(82) calculated by the Coats–Redfern, Kissinger, Ozawa and Horowitz–Metzger methods are given in Table 3. The activation energies evaluated by the Kissinger and Ozawa equations, 11.92 and 13.05 kcal mole, respectively, are comparable with the value, 12.93 kcal mole obtained from the water adsorption isotherms by a gravimetric method [3]. The activation energies by the Ozawa or Kissinger method are independent of heating rate and therefore more acceptable.

TABLE 2

Effect of heating rate on DTA peak temperature of FeNaY(82) sample

Heating rate (°C min^{-1})	DTA peak temperatures (°C)		
	First endotherm	Second endotherm	Third endotherm
2.5	90 and 170	280	
4.1	98 and 190	285	
5.3	160	295	400
8.0	165	300	410
10.0	165	300	415

TABLE 3

Activation energy for dehydration of FeNaY (82)

Method	Energy of activation for first endotherm (kcal mole^{-1})
1. Coats–Redfern	4.23
2. Coats–Redfern (modified)	2.00
3. Ozawa	13.05
4. Piloyan–Novikova	Not applicable
5. Kissinger	11.92
6. Horowitz and Metzger	7.45

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