

KINETICS OF WATER DESORPTION FROM PELLETIZED 4A AND 5A ZEOLITES

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ABSTRACT

Kinetic parameters (orders of desorption, pre-exponential factors and activation energies) are determined for the desorption of water from pelletized Linde 4A and 5A zeolites using temperature programmed desorption. The values of the parameters agree well with those in the literature.

INTRODUCTION

In spite of the widespread industrial use of 4A and 5A synthetic zeolites, there have been few studies of water desorption from those adsorbents. Since desorption of water is the main process occurring during activation of the adsorbent before use, a better understanding of this process may help in the design of plant start-up procedures.

The purpose of the present investigation was to determine kinetic parameters for the desorption of water from pelletized Linde 4A and 5A zeolites. Orders of desorption, pre-exponential factors and activation energies were obtained using temperature programmed desorption.

EXPERIMENTAL

Commercially manufactured Linde 4A and 5A zeolites were obtained for evaluation in the form of 0.0625-in pellets. Scanning electron micrographs of the 5A zeolite showed crystal sizes varying between 1.5 and 3.0 μm . No attempt was made to obtain the crystal size distribution. The Si/Al ratio was 1.05 for the zeolite crystals, as measured by energy-dispersive X-ray analysis.

Temperature programmed desorption spectra were obtained gravimetrically using a Cahn 2000 recording electrobalance interfaced with an IBM-XT

computer for data acquisition and analysis. In a typical run, a 200 mg zeolite sample (usually two or three pellets) in equilibrium with atmospheric water was put in a glass bucket hanging from the weighing arm of the recording electrobalance. Argon gas, purified by passage through a molecular sieve filter, flowed through the system at a superficial velocity of 350 cm s^{-1} . Previous experiments showed that desorption rates were independent of carrier gas flow rate for argon superficial velocities exceeding 300 cm s^{-1} . Temperatures were programmed to vary linearly between that ambient and 700 K at rates varying between 45 and 440 K h^{-1} . A chromel–alumel thermocouple placed a few millimetres from the glass bucket was used to measure sample temperatures. The effect of temperature on the measured sample weight, due to carrier gas density and viscosity changes, was assessed by running blanks with an empty glass bucket. A few runs were carried out using a UTI-100 C mass spectrometer to monitor desorption products. No mass peaks other than those corresponding to water were observed.

RESULTS AND DISCUSSION

Temperature programmed desorption (TPD) is an experimental kinetic technique which allows identification of different bonding sites and evaluation of the kinetic parameters associated with those sites. Originally developed for work with single crystals [1], it has been extended to the study of desorption from porous solids [2].

Under equilibrium conditions in ambient air, both 4A and 5A zeolite samples contained about 18% wt. of water. The rate of desorption of water from the 4A zeolite pellets as a function of sample temperature is shown in Fig. 1. A single large peak can be observed, suggesting that this zeolite presents a single type of site for water adsorption. The small shoulder observed at low temperatures should correspond to surface water, i.e. water adsorbed outside the zeolite crystals.

Using different heating rates, B , the maximum desorption rate occurs at different temperatures, T_M . For first order desorption, a plot of $2 \ln T_M - \ln \beta$ versus $1/T_M$ should yield a straight line with slope and intercept equal to E_d/R and $E_d/A_d R$ respectively [2]. Here, E_d is the activation energy for desorption, A_d is the pre-exponential kinetic factor and R is the gas constant. From the TPD spectra in Fig. 1 values of T_M and β were obtained to construct the plot in Fig. 2. Also shown in that figure are data reported in the literature for desorption of water from Linde 4A zeolite at heating rates between 300 and 2400 K/h^{-1} . Both sets of data lie along a single straight line. The values for A_d and E_d shown in Table 1 were obtained from the slope and intercept of this straight line.

The rate of desorption of water from 5A zeolite pellets versus sample temperature is shown in Fig. 3. Three adsorption states are evident. Compar-

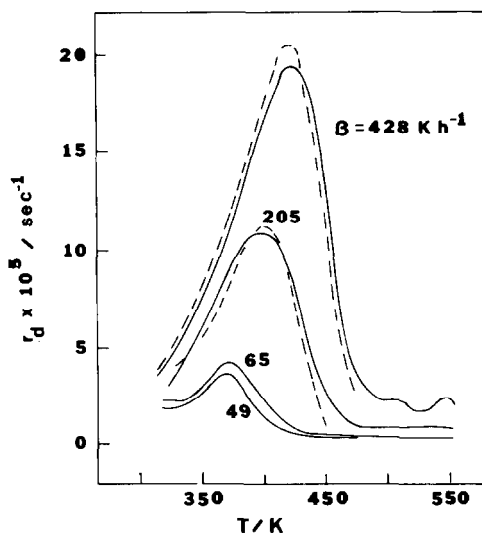


Fig. 1. Rate of water desorption, r_d , from pelletized Linde 4A zeolite versus temperature for the heating rates, β , indicated. Dashed curves were calculated from eqns. (1)–(4) with parameters from Table 1.

ing our TPD spectra with TPD spectra reported in the literature for water desorption from binderless 5A zeolite samples [4], we can assign the low temperature peak to water loosely held on the binder, while the other two peaks can be attributed to water held in the zeolite crystals. Since these

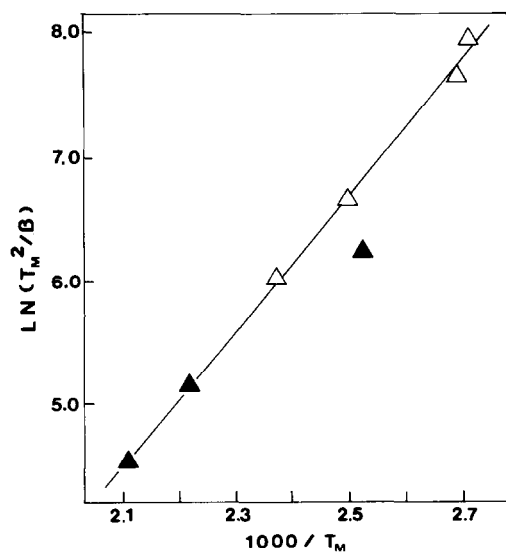


Fig. 2. Plot of $\ln T_M^2/\beta$ versus $1/T_M$. Open triangles denote data from Fig. 1, and filled triangles represent data from ref. 3. The slope of the straight line gives $E_d/R = 5540 \text{ K}$.

TABLE 1

Kinetic parameters for water desorption from 4A and 5A synthetic zeolites

Zeolite	Desorption peak	E_d (K)	A_d (s^{-1})	m_{0i}	Reference
Linde 4A	I	3090	19.1	0.031	this work
	II	5540	1950	0.13	this work
Linde 4A powder	II	5540	1950	—	Stakebake [3]
Linde 5A pellets	I	3090	19.1	0.031	this work
	II	6200	1.50×10^4	0.080	this work
Davidson 5A	III	8130	1.63×10^5	0.060	this work
	II	6200	7.50×10^4	—	Stakebake [4]
	III	8130	4.84×10^5	—	Stakebake [4]

peaks overlap considerably, kinetic parameters could not be obtained from a plot like Fig. 2. Instead, a non-linear curve fitting technique was used to fit the TPD spectra by solving the mass balance equations for adsorbed water

$$-dm_T/dt = r_d \quad (1)$$

$$r_d = \sum A_{di} \exp(E_{di}/RT) m_i \quad (2)$$

$$dT/dt = \beta \quad (3)$$

$$\text{for } t = 0, m_i = m_{0i}, T = 300 \text{ K} \quad (4)$$

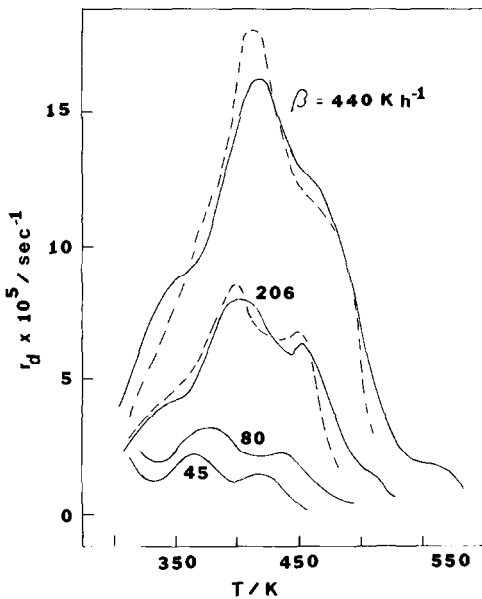


Fig. 3. Rate of water desorption r_d from pelletized 5A zeolite versus temperature for the heating rate, β , indicated. Dashed curves were calculated from eqns. (1)–(4) with parameters from Table 1.

where m_T is the mass of water adsorbed per unit mass of dry zeolite, m_i is the mass adsorbed in bonding site i , and r_d is the rate of desorption. Here we neglect readsorption of water and mass transfer resistances outside the zeolite crystals. A curve calculated from eqns. (1)–(4) with parameters from Table 1 is shown in Fig. 3. It should be noted that desorption rates spanning two orders of magnitude, and temperatures varying from ambient to over 700 K, can be fitted with a single set of rate parameters. Equations (1)–(4) were used to fit the TPD spectra for water desorption presented by Stakebake [4]. However, since his rates were reported in ‘arbitrary units’, our fitting technique was limited to adjustment of peak maxima and peak height ratios. The results obtained are presented in Table 1.

The values for the kinetic parameters obtained for water desorption from our zeolite pellets and those taken from the literature for water desorption from binderless zeolites are almost the same. This suggests that mass transfer resistances and readsorption on the binder have negligible effects on the kinetics of water desorption from the zeolite crystals.

The pre-exponential factors A_d listed in Table 1 are much smaller than a vibrational frequency, $\nu = 10^{13} \text{ s}^{-1}$. According to Gorte [5], small pre-exponential factors should be obtained for desorption from porous media when readsorption is important. In this case, A_d should be proportional to the ratio of the diffusion coefficient D to the square of the diffusion length l , D/l^2 . Assuming the crystal size distribution to be the same for the 4A and 5A zeolite pellets, we can estimate the diffusion coefficient for water to be one or two orders of magnitudes larger for 5A zeolite than for 4A zeolite crystals. We can compare this result with values of diffusion coefficients of hydrocarbons in 4A and 5A zeolites reported by Kärger and Caro [6]. For example, the ratio of the diffusion coefficients of butane in those zeolites is $D_{5A}/D_{4A} \approx 300$.

The population of bonding states II and III in the 5A zeolite crystals follow the distribution obtained by Stakebake [4]; that is, 57% of the water in the zeolite crystals is bound to site II while the remaining 43% is bound to site III. Stakebake suggests that site II corresponds to water bound to cations in the zeolite cages, while site III represents water held in a dodecahedral cluster in the large α cage.

CONCLUSION

We have measured desorption rates for water adsorbed in commercial 4A and 5A zeolite pellets. Results are reported in standard rate units, rather than the arbitrary units used by previous authors. A single rate expression, eqn. (2), with coverage-independent parameters fits those rates quantitatively. The values of the parameters agree well with literature data.

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