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THE KINETICS OF COMPLEX REACTIONS IN BOUNDARY PHASES

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An investigation was made into the interaction in an interphase boundary as a complex kinetic process composed of a series of elementary steps. The separation of some steps of a complex heterogenous process was carried out by means of the non-isothermal method.

A common reaction model for complex reactions in an interphase boundary was set up, along which processes take place as a series of consecutively parallel steps.

The application of Flynn and Wall's criterion indicated the predominant role of parallel steps in a complex mechanism. Kinetic parameters of activation energy, orders of reactions, and pre-exponential factors of individual steps were determined used Šestak's method.

INTRODUCTION

The recent introduction of non-isothermal methods into kinetic research has opened up new possibilities for research into heterogenous processes. A whole series of methods[1,2,3,4] has been developed. Using them, it is possible to establish the limiting process mechanism, as well as other kinetic processes, the activation energy, and the pre-exponential factor from thermo-analytic measurements. Relatively poorer results have been obtained from the heterogeneous processes, the process mechanisms of which are not dictated by one step, but by many. The first approach at studying the problems of such reactions was met in the works of Flynn and Wall[5], Koch[7], K.Heide[6].

Especially interesting for research of complex heterogene processes are desorption processes in boundary phases which are as a rule characterized by numerous elementary processes. One such model is represented by the water--zeolite system with several overlapping thermodesorptional peaks. The problem of the complex interaction of these systems is approached in various ways, with the result that for the sample NaX-H_2O, authors[10] establish the change in activation energy as a temperature function, while, seeing two peaks in

the sample CaA-H_2O[11], authors establish two processes, one of which is ascribed to macro pores, the other to micro pores.

The complexity of the problem is seen in the work of Kirchoff[12], from which originates the theory that under determined conditions, desorption processes can take place as a series of independent reactions.[13]

The reaction model

Qualitative works in the field of thermal analysis[8], as well as quantitative thermo-chemical works[14], show the phenomenon of differently bound types of water on zeolite surfaces. Depending on the type of zeolite cation, theree or four peaks can appear.

On the basis of these results as well as the results of NMR research which showed the existance of fast exchange between phases, the pollowing reaction model may be displayed:

$$\begin{array}{ccc} (ZH_2O)_i & \rightleftarrows & (ZH_2O)_{i-1} \\ \uparrow\downarrow & & \uparrow\downarrow \\ (H_2O)_g & & (H_2O)_g \end{array}$$

where $(ZH_2O)_i$ represents water in i bound state, i the number of differently bound water molecules; k_{i+} and k_{i-} correspond to the transition reactions from one state into another, while k_{ig+} and k_{ig-} correspond to the transition reactions from bound forms in gas desorption.

EXPERIMENTAL

The synthetic zeolites LiA, NaA, and KA were used in the work. NaA and KA are commercial samples produced by Union Carbide, while LiA was made up by ionic exchange from NaA[19]. Thermal analysis measurements were carried out on a Perkin-Elmer DSC-1B system, with a heating rate of 1^o per min. to 65^o per min.

Calculations were carried out on a PDP-11 computer.

RESULTS

Using the EGA method, water desorption from type-A zeolite with monovalent cations was investigated at various heating rates of 1^o per min. to 64^o per min. Fig. 1 shows the water desorption process from NaA zeolite. At low heating rates two maxima noticeably exist which merge when the heating rate increases and moves towards higher temperatures.

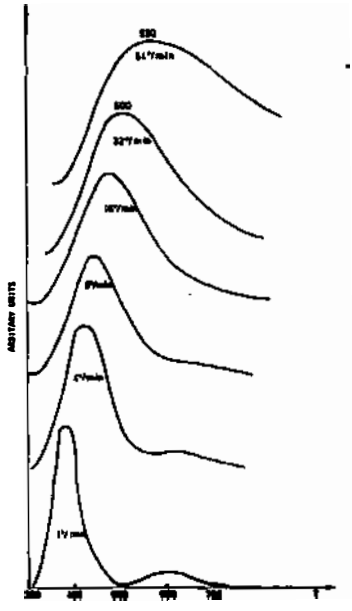

Fig.1. System NaA - H_2O, EGA et different heating rates.

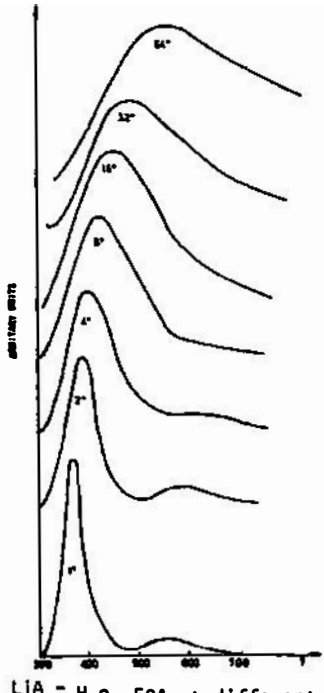

Fig. 2 System LiA - H_2O, EGA at different heating rates.

System LiA-H_2O also acts in a similar fashion, where again two peaks--the first of very large, the second of very small, intensty--can be seen. The first peak is somewhat narrower than the corresponding one in NaA. Potassium zeolite shows a substantial difference in comparison with LiA and NaA, since only one maximum appeared in it, broadening and moving towards higher temperatures as the heating rate increased.

For processes with low heating rates, where the resolution was at its greatest, a kinetic analysis using Šestak's[2] method was carried out, whereupon cases of well-known functional dependences $g(\alpha)$ were examined and the function $p(x)$ was calculated to be developed to the order of the fourth degree.[18]

Results of the kinetic analysis are given in Table 1, from which it can be observed that desorption processes can be very accurately described as reactions of the first order, since the regressional coefficients are very high.

Table 1

	E kcal/mol	Z sec^{-1}	n	R
LiA	9.8	8.5×10^5	1	0.998
	17.3	3.2×10^6	1	0.998
NaA	10.5	3.4×10^4	1	0.999
	19.8	3.5×10^6	1	0.997
KA	8.1	2.8×10^4	1	0.999

DISCUSSION AND CONCLUSION

Considering the demonstrated kinetic results with the given model, an analysis of several degrees is possible in the following way:

a) The reactions of readsorption k_{lg-} were not taken into consideration during the kinetic analysis, since the EGA was taken in a stream of dry nitrogen, ruling out the possibility of readsorption of desorbed water. The proof for the aforementioned conclusion lies in the fact that function linearity g(x) is estremely good--even at a low heating rate process--e.g. 1° per min.

b) An increase in process resolution, achieved by decreasing the heating rate, indicates the clear influence of the parallel steps which are demonstrated in the model by the reaction to which the constant k_{lg} corresponds.

This is in agreement with the example illustrated by Flynn and Wall[5], so that the desorption process in the case of LiA and NaA is considered to consist of two independent steps, whereas it consists of a single step in the case of KA. Kinetic parameters obtained for these processes, in the case of desorption which takes place at lower temperatures, show very close values which do not substantially differ from the enthalpy of water evaporation. Pre-exponential factors for these processes demonstrate the following regularity: for those processes characterized by the widest temperature dispersion (e.g.KA) pre-exponential values have the lowest values; for those processes charakterized by the narrowest dispersion (e.g. LiA), the highest values obtain.

c) A particularly sensitive problem in the given model presents itself in establishing the number of possible kinetic steps expressed by number i. In earlier works the number of processes was established by introducing the minimum number of gaussian functions criteria, with the sum of which it is possible to describe the experimentally given process with the greatest degree of accuracy. Thermo-chemical results gave very good results in those cases[14], while the kinetic constants in some examples obtained quite unrealistic values.

The gaussian approximation gives three elementary curves for NaA and LiA zeolite, while only two are obtained for KA. As, was reported in this paper, experements show that , two processes exist for the former, one for the latter. The reason for such behaviour can be twofold. The aforementioned fact that nitrogen is used in the experiment as a carrier gas points to the possibility that the low temperature process is such that the nitrogen "washes" it away to such an extent that its intensity is considerably reduced. In the work[6] it was shown that it is impossible to separate two consecutive steps if their activation enegies are very close. As shown by Fig. 4, two independent parallel reactions can behave in a similar way, and this possibility is very realistic in our case.

In concrete examples the most probable influence is that of the first and second enumerated reasons.

Since the method of various heating rates in the case of KA produced only one process for which kinetic parameters with very high regressional parameters were calculated, it was interesting to make the comparison of experimental movements at different heating rates and theoretically obtained curves for the given kinetic parameters.

The difference reflected in Fig. 3 leads to the conclusion that in addition to a very good agreement of experiments with Šestak's method, a concrete case one is not dealing with a single step.

To establish the possible number of steps, it is probably necessary to use stricter criteria--perhaps the minimum number of steps which yields the same kinetic parameters for different heating rates.

d) The question of the interexchange between differently bound water molecules--labelled in the reaction model with i and i-1, and dealt with by NMR works[15,16]--was subsequently shown to be insignificant in concrete cases. NMR results demonstrated that a phase exchange is minor only at temperatures below 210°K, but very rapid at temperatures of approximately 300°K; thus it may be expected that an exchange is even more rapid in the thermodesorption region but that a low heating rate from which kinetic parameters are calculated is sufficient for the system to establish equilibrium between the state and in relation to the state i-1.

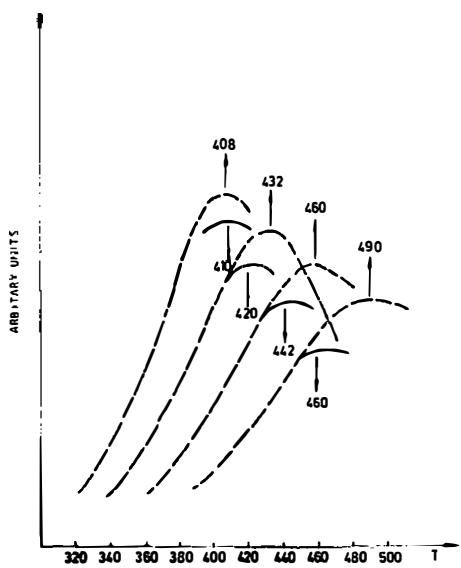

Fig.3. The comparison of a theoretically calculated process (represented by a dotted line) with a dehydration process, KA, at different heating rates.

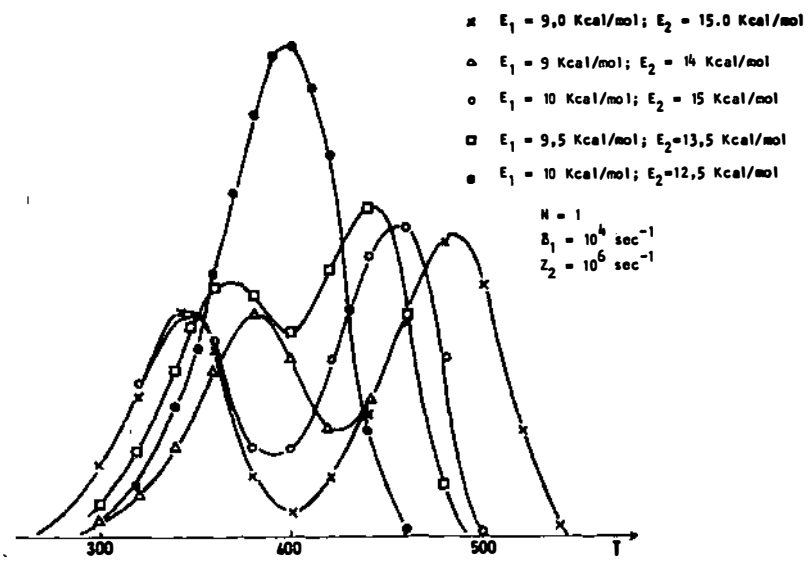

Fig. 4. Theoretically calculated independent parallel reactions

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