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NON-ISOTHERMAL DEHYDRATION KINETICS OF SOME CATIONITES

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Abstract

The kinetic parameters of dehydration were determined under non-isothermal conditions for different polystyrenedivinylbenzene sulfonic acid type cationites (DVB) and their dependence on the degree of cross-linking granulation, porosity, specific surface, content of SO_3M groups (M=Li, Na, K, Rb), nature of the alkali metal in partially neutralized $-SO_3H$ groups and heating rate was investigated.

Keywords: dehydration, DVB cationites, kinetic parameters, thermal stability

Introduction

Thermal stability and water content are important properties of polystyrene-divinylbenzene sulfonic acid type cationites (DVB) when they are used as catalysts in anhydrous organic media. Following our previous works [1–4], this paper presents a kinetic study of their non-isothermal dehydration. The purpose of this work is to investigate the influence of various physical characteristics of the cationites (granulation, metal content, etc.) on the kinetic parameters of dehydration.

Experimental

Macroreticulars-macroporous Amberlyst cationites in the acid form, or partially neutralized with alkali metals (Li, Na, K, Rb), as supplied by Rohm & Hass, USA, as well as gel cationites in the acid form, with different degrees of cross-linking Dowex 50 W type, produced by Bio-Rad-Laboratory, USA have

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been used. In some experiments Romanian cationites, Vionit CS-31 type, have also been used.

All the cationites have been well characterised concerning their granulation, porosity, degree of cross-linking acidity and *M* content, and water content as given elsewhere [1–3].

The mass loss of each cationite, under controlled heating TG curves was recorded on a Paulik-Paulik-Erdey Derivatograph (MOM, Budapest) using platinum crucibles and dried Al_2O_3 as reference. In almost all the experiments, we used static air atmosphere, but some tests were also conducted in an argon (~0.1% O_2) or nitrogen atmosphere (~0.3% O_2).

The specific surface of macroporous cationites was determined with a Carlo-Erba Sorptomatic equipment, by nitrogen adsorption at liquid nitrogen temperature.

The total and remnant acidity in mmol g^{-1} was determined by acid-base titration.

The granulation was evaluated by sieving, according to the granulated fractions. The samples of cationic catalysts with different $-SO_3H/-SO_3M$ ratios were obtained by equilibrating the granules of $-SO_3H$ form with aqueous solutions containing known M^+/Cl^- and H^+/Cl^- ratios (where $M=Li^+, Na^+, K^+, Rb^+$). The contents in $-SO_3H$ groups in the samples were evaluated from the difference between the initial and final acidity.

Results and discussion

The thermal behaviour of cationites up to 500°C has been presented previously [4]. The endothermic effect between 100 and 130°C, has been attributed to the dehydration process of mono- or di-hydrated styrenedivinylbenzene sulfonic acid polymers, as also suggested by the results obtained for samples which have been dried in an oven at 100°C, or in air at ambient temperature.

In the present work we studied the non-isothermal kinetics of the dehydration process by evaluating its kinetic parameters: reaction order, *n*, activation energy, *E*, and the preexponential factor, Z_α. As discussed in many other papers, it is difficult to ascribe a certain meaning to the three parameters calculated from a non-isothermal experiment [5, 6]. For this reason, we shall consider them as being apparent parameters throughout the present paper.

The dehydration process of the poly-styrenedivinylbenzene sulfonic acid type cationites, under non-isothermal heating conditions, can be described as follows:

$$\underset{1-x}{R{-}SO_3H\cdot mH_2O_{(s)}} \rightarrow \underset{x}{R{-}SO_3H_{(s)} + mH_2O_{(g)}} \tag{1}$$

In order to evaluate the kinetic parameters we used an integral method given in [7]:

$$\ln\int_0^\alpha \frac{\mathrm{d}x}{f(x)} - s\ln T = -\frac{E}{RT} + \ln Z_\alpha - \ln\beta + L(s), \quad s \in \{0,1,2\} \qquad (2)$$

where $F(\alpha)=\int_0^\alpha \mathrm{d}x/(f(x)$ is the integral function of conversion, $L(s)$ is a correction factor, E is the apparent activation energy in kJ mol^{-1}, Z_α is the apparent pre-exponential factor in min^{-1} and β is the constant heating rate in K min^{-1}.

For the purpose of this work we used $s=0$ and $L(0)=(\ln E/R-5.33)$ and the polynomial form of the differential function of conversion, $f(\alpha)=(1-\alpha)^n$, where n is the apparent order of the reaction. The plot of $\ln F(\alpha)$ *vs.* $1/T$ leads to a straight line for a proper value of the reaction order, n. The values of the other two kinetic parameters, E and Z_α, are selected from the slope and intercept, respectively, for an apparent order of reaction, ranging from 0 to 5 by using a computer programme which searches for the maximum of the linear correlation factor, r.

The effects of the various physical characteristics of the cationites on the values of the apparent kinetic parameters of the dehydration reaction are dealt with below.

Effect of the degree of cross-linking

In Table 1, we present the effect of the degree of cross-linking on the dehydration kinetics of gel cationites Dowex 50W with granulation between 0.284–0.417 mm.

Table 1 Dependence of the kinetic parameters of the dehydration of gel-type acid cationites (Dowex) on the degree of cross-linking for the granulation range 0.284–0.417 mm

No.	Cationite	β/ K min^{-1}	Total acidity*	Mass loss**	n	E/ kJ mol^{-1}	Z_α/ s^{-1}	r
1	50W×12	2.5	5.10	2.01	2.1	19.8	$1.90\cdot10^8$	0.998350
2	50W×8	2.5	5.20	2.01	2.2	19.8	$1.65\cdot10^8$	0.999831
3	50W×4	2.5	5.36	2.05	2.3	19.7	$1.50\cdot10^8$	0.999730
4	50W×2	2.5	5.76	1.92	2.1	20.1	$3.05\cdot10^8$	0.999369

* mequiv g^{-1}
** mol H_2O per gequival SO_3H

At a heating rate of 2.5 K min^{-1} (the slowest one under our experimental conditions) for some samples of cationite dihydrates, dried in air, a change of the degree of cross-linking from 12% DVB to 2% DVB did not affect significantly the apparent kinetic parameters of the dehydration of sulfonic acid cationites of Dowex 50W type: n increased from 2.1 to 2.3, E was 19.7–20.1 kJ mol^{-1} and Z_α had values between $1.5–3\cdot10^8$ s^{-1}.

Effect of granulation

The effect of granulation on the apparent kinetic parameters was studied at a heating rate of 10 K min^{-1}, for the acid cationite Amberlyst-15 type, and is shown by the values of n, E and Z_α as given in Table 2.

Table 2 Dependence of the kinetic parameters of the dehydration of the Amberlyst-15 cationite on the granulation

No.	Granulation/ mesh	β/ K min^{-1}	Total acidity*	Mass loss**	n	E/ kJ mol^{-1}	Z_α/ s^{-1}	r
1	28–35	283	4.71	2.20	2.8	38.1	$3.2\cdot10^{20}$	0.997205
2	35–50	283	4.71	2.20	1.3	15.1	$2.2\cdot10^{5}$	0.997260

* mgequival g^{-1}
** mol H_2O per gequival SO_3H

For an increase of granulation from 35–50 mesh to 28–35 mesh, n increases from 1.3 to 2.8, E from 15.1 to 38.1 kJ mol^{-1} and Z_α from $2.2\cdot10^5$ to $3.2\cdot10^{20}$ s^{-1}. We assume that this fact may be due to a strong superposition of the physical process of diffusion over the dehydration.

Effects of the specific surface and porosity

At a heating rate of 10 K min^{-1} the results given in Table 3 were obtained for some macroreticular-macroporous cationites as Amberlyst and for the Vionit CS-31 type, with different values of specific surface and porosity.

Table 3 Dependence of the kinetic parameters of the dehydration of macroreticular Amberlyst cationites on the specific surface and porosity

No.	Cationite	β/ K min^{-1}	Mean pore diameter/ Å	Specific surface/ m^2 g^{-1}	n	E/ kJ mol^{-1}	Z_α/ s^{-1}	r
1	XN-1008	10	125	3.8	2.2	24.9	$3.20\cdot10^{10}$	0.999547
2	XN-1010	10	51	6.8	2.0	35.8	$1.10\cdot10^{7}$	0.999205
3	XN-1005	10	175	115.3	2.0	15.9	$3.34\cdot10^{6}$	0.996000
4	15	10	265	41.4	1.3	15.1	$2.20\cdot10^{5}$	0.997260
5	CS-31*	10	60	3.8	2.5	17.7	$6.80\cdot10^{6}$	0.999505

* Vionit type cationite

One may notice an increase in the value of n when the mean pore diameter decreases from ~265 Å (Amberlyst-15) to ~51 Å (Amberlyst XN 1010). Also, the apparent activation energy increases from 15.1 to 35.8 kJ mol^{-1} and Z_α increases from $2.2 \cdot 10^5$ to $1.1 \cdot 10^7$ s^{-1}.

The Amberlyst XN 1008 cationite with n=2.2, E=24.9 kJ mol^{-1} and $Z_\alpha = 3.2 \cdot 10^{10}$ s^{-1} does not fit in the above dependencies, possibly because the superposition of the diffusion process over the process of the dehydration is more pronounced for a cationite with smaller porosity and specific surface.

Effect of the nature and concentration of the metal present in the cationite

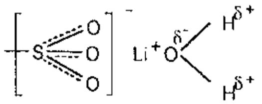
The analysis of macroreticular-macroporous cationites of the Amberlyst-15 type partially neutralized with alkali metals (Rb, K, Na, Li) revealed that the apparent kinetic parameters depend on the nature (Table 4) and concentration (Tables 5a–d) of the metal.

Table 4 Effect of the nature of metal on sulfonic acid groups on the kinetic parameters of the dehydration of the cationite Amebrlyst-15 (granulation 35–50 mesh)

No.	M	Metal content/ % equival	β/ K min^{-1}	n	E/ kJ mol^{-1}	Z_α/ s^{-1}	r
1	Rb	46.8	2.5	2.8	24.9	$9.00 \cdot 10^{11}$	0.999724
2	K	47.6	2.5	3.9	25.7	$1.80 \cdot 10^{12}$	0.999337
3	Na	54.9	2.5	1.8	18.5	$4.15 \cdot 10^7$	0.999697
4	Li	48.9	2.5	2.7	18.8	$7.00 \cdot 10^7$	0.999014
5	H	0	2.5	3.1	19.5	$7.20 \cdot 10^7$	0.999400

At a heating rate of 2.5 K min^{-1} a decrease was observed in the value of the apparent activation energy from 24–25 kJ mol^{-1} for Rb and K, to 18–19 kJ mol^{-1}, for Na and Li, which means that E decreases as the size of the metal ion decreases for some metals of comparable concentrations in the cationite. Similarly, the nature of the metal influences also the value of the Z_α parameter. It is to be mentioned that cationites partially neutral by metals and dried in air at the usual temperature exhibited different water losses. Thus, those neutralized with Rb and K lost ~1.5 moles of H_2O while those neutralized with Li and Na and the acid samples lost 2–2.5 moles of H_2O per g equivalent of SO_3^- .

We consider that the stronger hydration for the case of Li and Na cationites than for those of K and Rb may be explained on the basis of Zundel and Murr's results [8]. They observed that the SO_3Li monohydrated groups can be considered as being of proton donating-accepting structure, according to the following picture:



A polarized water molecule may be bound easily to other water molecules through a hydrogen bond, thus contributing to a stronger hydration of the cationite. It is obvious that a water molecule which is linked by hydrogen bond to the cationite $H_2O–H_2O$ should be eliminated more easily, with lower values of the apparent kinetic parameters (see lines 3, 4, 5 in Table 4).

Table 5a Effect of the Rb^+ content in the sulfonic acid groups on the dehydration kinetics of Amberlyst-15 in the H–Rb form

No.	Rb^+ content/ % equiv	β/ K min^{-1}	n	E/ kJ mol^{-1}	Z_α/ s^{-1}	r
1	35.6	2.5	2.3	22.5	$1.20\cdot10^{10}$	0.999893
2	46.8	2.5	4.0	24.9	$9.00\cdot10^{11}$	0.999724
3	84.2	2.5	4.0	25.4	$1.45\cdot10^{12}$	0.999795

Table 5b Effect of the K^+ content in the sulfonic acid groups on the dehydration kinetics of Amberlyst-15 in the H–K form

No.	K^+ content/ % equiv	β/ K min^{-1}	n	E/ kJ mol^{-1}	Z_α/ s^{-1}	r
1	23.2	2.5	1.9	21.1	$1.25\cdot10^{9}$	0.998931
2	47.6	2.5	3.9	25.7	$1.80\cdot10^{12}$	0.999337
3	59.7	2.5	3.8	26.7	$7.50\cdot10^{12}$	0.998434

Table 5c Effect of the Na^+ content in the sulfonic acid groups on the dehydration kinetics of Amberlyst-15 in the H–Na form

No.	Na^+ content/ % equiv	β/ K min^{-1}	n	E/ kJ mol^{-1}	Z_α/ s^{-1}	r
1	29.0	2.5	1.8	18.4	$3.80\cdot10^{7}$	0.999753
2	54.9	2.5	1.8	18.5	$4.15\cdot10^{7}$	0.999697
3	77.6	2.5	4.4	26.2	$4.80\cdot10^{12}$	0.999776

Table 5d Effect of the Li^+ content in the sulfonic acid groups on the dehydration kinetics of Amberlyst-15 in the H–Li form

No.	Li^+ content/ % equiv	β/ K min^{-1}	n	E/ kJ mol^{-1}	Z_α/ s^{-1}	r
1	21.82	5	2.0	18.4	$2.8\cdot10^{7}$	0.999550
2	48.99	5	2.5	19.4	$9.2\cdot10^{6}$	0.998445
3	54.93	5	2.2	18.2	$3.3\cdot10^{7}$	0.999694

An increase in the metal concentration, in the case of Na, K and Rb, contributes to the increase of the values of the apparent kinetic parameters n, E and Z_α. The reaction order, n, ranges from 1.8 to 4.4, E from 18.4 to 26.7 kJ mol^{-1} and Z_α from ~10^7 to 10^{12} s^{-1}.

Effect of the heating rate

The effect of the heating rate on the values of the apparent kinetic parameters of the dehydration of Dowex 50W cationite is presented in Table 6a, and the effect on the kinetics of the dehydration of macroreticular-macroporous cationites type Amberlyst-15 in the acid form and partially neutralized with alkali metals (Rb, K, Li, Na) is presented in Table 6b.

Table 6a Effect of the heating rate on the non-isothermal dehydration kinetics of gel type Dowex cationites

No.	Cationite type	Degree of cross-linking/ % DVB	β/ K min^{-1}	n	E/ kJ mol^{-1}	Z_α/ s^{-1}	r
1	50W×12	12	10	1.8	16.9	$4.20\cdot10^{6}$	0.997676
			5	2.0	18.1	$1.80\cdot10^{7}$	0.999762
			2.5	2.5	21.6	$2.80\cdot10^{9}$	0.998586
2	50W×8	8	10	2.2	19.6	$1.62\cdot10^{8}$	0.999102
			5	2.0	18.9	$3.70\cdot10^{7}$	0.999923
			2.5	2.2	19.8	$1.65\cdot10^{8}$	0.999831
3	50W×4	4	10	1.8	15.3	$1.00\cdot10^{5}$	0.999411
			5	2.3	19.6	$1.20\cdot10^{8}$	0.999457
			2.5	2.3	19.7	$1.50\cdot10^{8}$	0.999730
4	50W×2	2	10	2.0	18.5	$2.20\cdot10^{7}$	0.999184
			5	1.9	18.3	$2.00\cdot10^{7}$	0.999124
			2.5	2.1	20.1	$3.05\cdot10^{8}$	0.999369

In most cases, an increase in the heating rate from 2.5 to 10 K min^{-1}, leads to a decrease in the apparent kinetic parameters. As shown in Table 6a, the apparent reaction order for the dehydration of gel cationites n, ranges from 2.5 to 1.8, the apparent activation energy, E, from 15.3 to 21.6 kJ mol^{-1} and the apparent pre-exponential factor, Z_α, from $4.5\cdot10^5$ to $2.8\cdot10^9$ s^{-1}.

The data in Table 6b show that for macroreticular-macroporous cationites n ranges from 4.4 to 1.2, for cationites partially neutralized by alkali metals and acid Amberlyst-15 from 1.5 to 2.3.

Table 6b Effect of the heating rate on the dehydration kinetics of some macroporous cationites

No.	Cationite type	Metal content/ % equival	β/ K min^{-1}	n	E/ kJ mol^{-1}	Z_α/ s^{-1}	r
1	Amberlyst Rb	46.80	10	1.2	17.1	$5.80\cdot10^{6}$	0.999815
			5	1.8	18.9	$1.10\cdot10^{8}$	0.999677
			2.5	2.8	24.9	$9.00\cdot10^{11}$	0.999724
2	Amberlyst K	59.70	10	2.6	20.4	$1.14\cdot10^{9}$	0.999755
			5	2.8	21.7	$3.90\cdot10^{9}$	0.999245
			2.5	3.7	26.3	$3.85\cdot10^{12}$	0.999187
3	Amberlyst Na	77.60	10	2.4	18.3	$3.60\cdot10^{7}$	0.999426
			5	2.8	20.9	$1.60\cdot10^{9}$	0.999890
			2.5	4.4	26.2	$4.80\cdot10^{12}$	0.999776
4	Amberlyst Li	54.93	10	2.0	17.5	$2.00\cdot10^{7}$	0.999282
			5	2.2	18.2	$3.30\cdot10^{7}$	0.999694
			2.5	3.6	22.4	$1.70\cdot10^{10}$	0.999415
5	Amberlyst 15	0.00	11.7	1.5	15.2	$7.30\cdot10^{6}$	0.999400
			7.7	1.7	16.1	$1.30\cdot10^{7}$	0.999700
			2.8	2.3	17.9	$2.30\cdot10^{8}$	0.999800

For Amberlyst-15 the apparent activation energy ranges from 15.2 kJ mol^{-1} for a heating rate of 11.7 to 26.3 kJ mol^{-1} for a heating rate of 2.5 K min^{-1}. The values of the apparent pre-exponential factor, Z_α, change as well.

This dependence of the apparent kinetic parameters on the heating rate seems to reveal a greater complexity of the dehydration process than that described by Eq. (1). In fact, we suppose that dehydration and diffusion occur simultaneously and the two processes compete with each other. This competition might explain the strong dependence of the apparent kinetic parameters on the heating rate.

Zundel and co-workers provided some more results which support the observation that the kinetics of dehydration changes with the heating rate [8]. They concluded that a cationite is dried completely when a high heating rate is used, but the same substance does not ever lose its last water molecule if the heating rate is low.

As we have pointed out, the values of the apparent kinetic parameters also depend on the degree of cross-linking specific surface and porosity of the cationite. This fact seems to sustain our supposition of the dehydration – diffusion competition.

Conclusions

The kinetics of the non-isothermal dehydration of some cationites was studied. The values of the apparent kinetic parameters, i.e. reaction order, n, activation energy, E and pre-exponential factor, Z_α, for the dehydration of the polystyrenedivinylbenzene sulfonic and cationites, were calculated by an integral method. The results listed in several tables revealed a strong influence of the experimental parameters (heating rate) as well as of the physical characteristics of the cationites (porosity, specific surface, granulation, degree of cross-linking) upon the macro kinetics, which allowed us to conclude that the studied non-isothermal dehydration is, in fact, a superposition of a diffusion process over the chemical process described by Eq. (1).

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