KINETICS OF NON-ISOTHERMAL BEHAVIOUR OF SYNTHETIC CATIONITES WITH LOW ACIDITY

C. Iditoiu[1], E. Segal[2] and D. Chambrée[1]*

[1]Aurel Vlaicu University, Bd. Revolutiei 81, 2900 Arad
[2]University of Bucharest, Bd. Republicii 13, Bucharest, Romania

Abstract

An investigation was made of the thermal behaviour under non-isothermal conditions of a series of low-acidity synthetic cationites having a methacrylic–divinylbenzene (DVB) matrix, such as Amberlite IRC 120, Ionenaustauscher IV Merck, Vionit CC1, and Purolite C104, C105 and C106. The macroporous, macroreticular and gel cationites were in acidic or sodium form, with various granulations and degrees of cross-linking. The apparent kinetic parameters (reaction order, n, activation energy, E, and pre-exponential factor A) were evaluated for two dehydration processes and the effects of the experimental conditions on these parameters were investigated.

Keywords: cationite thermal analysis, low-acidity ion-exchangers, non-isothermal dehydration kintics, thermal behaviour of synthetic resins

Introduction

Commercial ion-exchange resins of different types and with different characteristics are frequently used as ion-exchangers and/or catalysts [1]. Some studies [2] have suggested carboxylic cationites as potential catalysts in the food industry. However, in most cases their use as catalysts is limited by their relatively low thermal stability. Hence, a study of the thermal behaviour of carboxylic cationites under non-isothermal conditions has been undertaken. As a follow-up to our previous work [3, 4], this study deals with the general thermal behaviour of carboxylic cationites under non-isothermal conditions up to 500°C, and with the kinetics of the dehydration processes characteristic of the first two of the four observed decomposition steps.

Experimental

Macroporous, macroreticular or gel carboxylic cationites with various degrees of cross-linking (%DVB) and granulations, in acidic (H^+) and sodium (Na^+) form were investigated Purolite C104, C105 and C106, Amberlite IRC 120, Ionenaustauscher IV Merck and Vionit CC1. These commercial products were treated as follows: water washing, air drying, sieving according to their granulated fractions, washing with methanol, acetone and distilled water, change to the Na^+ form, change

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* Author to whom all correspondence should be addressed.

to the H^+ form, deionized water washing and air drying to constant mass. The ex-
change capacities of all materials were measured by acid-base titration. The mass
loss of each cationite under controlled heating was recorded on a Q Derivatograph
(MOM, Budapest), using a ceramic crucible and calcined Al_2O_3 as reference. All ex-
periments were conducted in air at a heating rate of 2.5, 5 or 10 K min^{-1} up to 500°C
(773 K). Illustrative TG/DTA curves are given in Fig. 1, for Ionenaustauscher IV
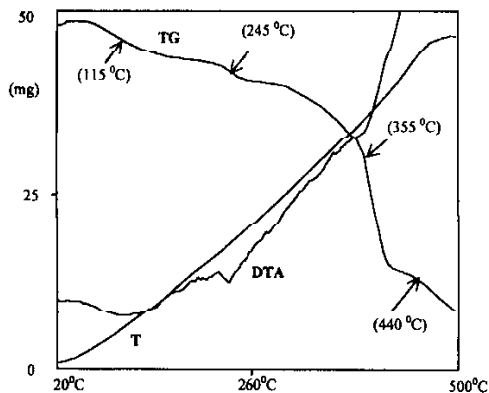Merck cationite in H^+ form with a granulation of 30-35 mesh.

Fig. 1 TG/DTA curves Ionenaustauscher IV Merck cationite. Sample mass: 44.4 mg; Tem-
perature range: 25–500°C; β=10 K min^{-1}; DTA: 100 μV

In order to confirm the dehydration processes which occur in the temperature
range 100–240°C, IR spectroscopy was used in addition to thermal analysis. The IR
spectra in KBr pellets of several air-dried samples heated to 250°C were recorded.

Results and discussion

Main characteristics

Table 1 presents the main characteristics of the studied low-acidity cationites.

Thermal effects

The four decomposition steps up to 500°C of the low-acidity cationites in both H^+
and Na^+ form are detailed in Table 2.

The first step, located between 100 and 120°C (column 3), is due to the loss of
adsorbed water molecules. A possible explanation of the second decomposition step,
observed in the range 240–280°C is intermolecular water elimination between two
neighboring carboxyl (–COOH) groups. This assumption was supported by our IR
spectra results for air-dried samples heated up to 250°C. The characteristic –OH IR
band of the –COOH group diminished or disappeared after heating of the samples.

Table 1 Characteristics of the analyzed carboxylic cationites

Cationite	Ionic form	Cross–linking degree/ %DVB[b]	Exchange capacity $meq\ g^{-1}$	Granulation/ mesh[a]	Porosity
Amberlite IRC 120	H+ Na+a	>20	10[b]/9.93[a]	20–30 35–50	macroporous macroreticular
Ionenaustauscher IV Merck	H+	18	10b/9.43[a]	16–30 30–35 35–50	macroporous macroreticular
Purolite C 104	H+ Na+a	12	9.2b/9.11[a]	14–50	macroporous
Purolite C 106	H+ Na+a	10	9.2b/9.09[a]	14–50 30–50	macroporous
Vionit CC1	H+	8	10b/9.71[a]	60–70	macroporous
Purolite C 105	H+ Na+a	7.2	9.5b/9.41[a]	14–50	gel

[a] Experimentally measured values; [b] Values taken from technical books

Table 2 Dependence of decomposition steps and mass losses in air on cationite type [a]

Cationite	Ionic form	Cross linking degree/ %DVB	Step 1			Step 2			β/ K min^{-1}
			T/°C	Mass loss/ %[b]	Mass loss (moles H2O) eqval COOH[c]	T/°C	Mass loss/ %[b]	Mass loss (moles H2O) eqval COOH[c]	
Amberlite IRC 120 35–50 mesh	H+	>20	105	22.8	1.27	–	–	–	5
	Na+	>20	100	14.2	0.77	–	–	–	
Ionenaustauscher IV Merck 35–50 mesh	H+	13	100	10.8	0.81	240	5.49	0.31	5
Purolite C 104	H+	12	120	9.2	1.56	270	12.9	0.78	
14–50 mesh	Na+	12	120	7.9	0.46	280	12.6	0.76	5
Purolite C 106 14–50 mesh	Na+	10	120	6.6	0.38	280	12.1	0.73	5
Vionit CC1 30–50 mesh	H+	8	100	6.7	0.36	250	15.2	0.86	5
Purolite C 105	H+	7.2	120	5.9	0.50	280	17.6	1.04	
14–50 mesh	Na+	7.2	120	4.9	0.28	270	17.3	1.01	5

Table 2 Continued

Cationite	Ionic form	Cross linking degree/ %DVB	Step 3			Step 4			β/ K min⁻¹
			$T/°C$	Mass loss/ %[b]	Mass loss (moles H_2O) eqval COOH[c]	$T/°C$	Mass loss/ %[b]	Mass loss (moles CO_2) eqval COOH[c]	
Amberlite IRC 120 35–50 mesh	H⁺	>20	–	–	–	445	9.7	0.42	5
	Na⁺	>20	–	–	–	430	8	0.32	
Ionenaustauscher IV Merck 35–50 mesh	H⁺	18	350	16.9	0.48	430	37	0.39	5
Purolite C 104 14–50 mesh	H⁺	12	370	18.2	0.45	460	38.1	0.94	
	Na⁺	12	360	13.8	0.38	430	32.3	0.80	5
Purolite C 106 14–50 mesh	Na⁺	10	360	14.1	0.34	460	34.2	0.84	5
Vionit CC1 30–50 mesh	H⁺	8	360	11.5	0.37	450	39.5	0.64	5
Purolite C 105 14–50 mesh	H⁺	7.2	370	11.4	0.39	460	19.1	0.65	5
	Na⁺	7.2	350	11.2	0.28	435	28.6	0.62	

[a] The temperature was varied between 20 and 500°C; [b] % from initial mass; [c] calculated from exchange capacity and mass loss

The third and fourth decomposition steps, located between 350 and 370°C and between 430 and 460°C, respectively, were presumed to be due to a CO_2 elimination coupled with oxidative depolymerization and polymeric matrix destruction.

Table 2 shows that the second and third steps are missing for the macroporous-macroreticular Amberlite IRC 120 (>20% DVB) cationite in both the H^+ form and the Na^+ form. This behaviour might be explained by steric hindrance of the proximate carboxylic groups to the elimination of water because of the high cross-linking.

Effect of the cross-linking degree

The dehydration kinetic parameters of low-acidity cationites in H^+ or Na^+ form, with a granulation of 35–50 mesh, are presented in Table 3.

The apparent kinetic parameters n, E and A of the two dehydration processes were evaluated by using a computer program. The values were selected for apparent reaction orders n ranging from 0 to 3, in steps of 0.01, after maximization of the linear correlation factor r, using the Coats-Redfern, Flynn-Wall [5] and modified Coats-Redfern methods with the conversion function form as follows:

$$n \neq 1 \qquad F(\alpha) = \frac{1 - (1 - \alpha)^{1-n}}{1 - n}$$

$$n = 1 \qquad F(\alpha) = -\ln(1 - \alpha) \tag{1}$$

Tables 3–5 contain only the results given by the modified Coats-Redfern method, for this gave values intermediate between those of the Coats-Redfern method
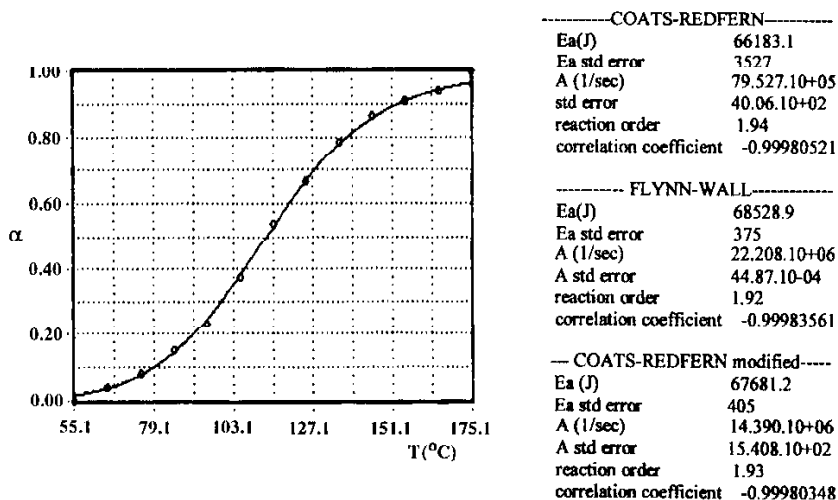


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----------COATS-REDFERN----------
Ea(J)                      66183.1
Ea std error               3527
A (1/sec)                  79.527.10+05
std error                  40.06.10+02
reaction order             1.94
correlation coefficient    -0.99980521

---------- FLYNN-WALL-------------
Ea(J)                      68528.9
Ea std error               375
A (1/sec)                  22.208.10+06
A std error                44.87.10-04
reaction order             1.92
correlation coefficient    -0.99983561

— COATS-REDFERN modified-----
Ea (J)                     67681.2
Ea std error               405
A (1/sec)                  14.390.10+06
A std error                15.408.10+02
reaction order             1.93
correlation coefficient    -0.99980348
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Fig. 2 Apparent kinetic parameters for the first step of dehydration of Ionenaustauscher IV Merck cationite

Table 3 Kinetics of cationite dehydration. Effects of cross-linking degree on kinetic parameters[a]

Cationite	Ionic form	Cross linking degree/%DVB	Sample mass/mg	β/K min⁻¹	Step 1 (100–120°C) Coats–Redfern modified	Step 2 (240–280°C) Coats–Redfern modified
Amberlite IRC 120	H^+	>20	60	5	$E=76.7\ kJ\,mol^{-1}$ $A=49.1\cdot10^1\ s^{-1}$ $n=2.06$ $r=-0.9962$	–
	Na^+	>20	56	5	$E=67.4\ kJ\,mol^{-1}$ $A=12.9\cdot10^6\ s^{-1}$ $n=1.42$ $r=-0.9970$	–
Ionenaustauscher IV Merck	H^+	18	50	5	$E=72.8\ kJ\,mol^{-1}$ $A=15.2\cdot10^1\ s^{-1}$ $n=1.83$ $r=-0.9998$	$E=161.0\ kJ\,mol^{-1}$ $A=56.2\cdot10^{13}\ s^{-1}$ $n=129$ $r=-0.9997$
Vionit CC1	H^+	12	51	5	$E=59.8\ kJ\,mol^{-1}$ $A=94.3\cdot10^1\ s^{-1}$ $n=2.05$ $r=-0.9994$	$E=160.0\ kJ\,mol^{-1}$ $A=58.5\cdot10^{12}\ s^{-1}$ $n=118$ $r=-0.9991$

[a] The granulation of samples was in the range 35–50 mesh

Table 4 Kinetics of cationite dehydration. Effects of granulation on kinetic parameters[a]

Cationite	Cross linking degree/ %DVB	Granulation/ mesh	Sample mass/ mg	β/ K min⁻¹	Step 1 (100–120°C) Coats–Redfern modified		Step 2 (240–280°C) Coats–Redfern modified	
Amberlite IRC 120	>20	20–30	54	2.5	$E=81.6$ kJ mol⁻¹ $A=22.9 \cdot 10^8$ s⁻¹	$n=1.95$ $r=-0.9995$		
		35–50	57	2.5	$E=79.9$ kJ mol⁻¹ $A=18.5 \cdot 10^7$ s⁻¹	$n=2.03$ $r=-0.9945$		
Ionenaustauscher IV Merck	18	16–30	48	2.5	$E=67.1$ kJ mol⁻¹ $A=14.4 \cdot 10^6$ s⁻¹	$n=1.60$ $r=-0.9967$	$E=163.9$ kJ mol⁻¹ $A=20.8 \cdot 10^{13}$ s⁻¹	$n=1.26$ $r=-0.9971$
		30–35	50	2.5	$E=52.1$ kJ mol⁻¹ $A=5.60 \cdot 10^3$ s⁻¹	$n=1.50$ $r=-0.9968$	$E=175.3$ kJ mol⁻¹ $A=53.3 \cdot 10^{13}$ s⁻¹	$n=1.12$ $r=-0.9998$
Vionit CC1	8	30–50	49	2.5	$E=62.8$ kJ mol⁻¹ $A=69.7 \cdot 10^5$ s⁻¹	$n=2.04$ $r=-0.9982$	$E=192.4$ kJ mol⁻¹ $A=47.5 \cdot 10^{14}$ s⁻¹	$n=1.02$ $r=-0.9960$
		60–70	51	2.5	$E=48.5$ kJ mol⁻¹ $A=12.5 \cdot 10^3$ s⁻¹	$n=2.07$ $r=-0.9991$	$E=168.2$ kJ mol⁻¹ $A=28.7 \cdot 10^{13}$ s⁻¹	$n=0.97$ $r=-0.9989$

[a] Carboxylic cationites were in H⁺ form

Table 5 Kinetics of cationite dehydration. Effects of heating rate on kinetic parameters [a]

Cationite	Cross linking degree/%DVB	Ionic form	Sample mass/mg	β/K min^{-1}	Step 1 (100–120°C) Coats–Redfern modified	Step 2 (240–280°C) Coats–Redfern modified
Purolite C 104 macroporous	12	H$^+$	42	2.5	$E=45.7$ kJ mol^{-1}; $A=25.2\cdot10^2$ s^{-1}; $n=1.58$; $r=-0.9993$	$E=931.4$ kJ mol^{-1}; $A=92.9\cdot10^4$ s^{-1}; $n=0.81$; $r=-0.9990$
		H$^+$	40	10	$E=37.3$ kJ mol^{-1}; $A=10.5\cdot10^1$ s^{-1}; $n=1.42$; $r=-0.9993$	$E=310.8$ kJ mol^{-1}; $A=25.8\cdot10^{26}$ s^{-1}; $n=2.4$; $r=-0.9919$
		Na$^+$	44	2.5	$E=44.2$ kJ mol^{-1}; $A=20.1\cdot10^2$ s^{-1}; $n=1.12$; $r=-0.9957$	$E=123.8$ kJ mo^{-1}; $A=79.3\cdot10^7$ s^{-1}; $n=1.06$; $r=-0.9987$
		Na$^+$	50	5	$E=38.2$ kJ mol^{-1}; $A=24.4\cdot10^1$ s^{-1}; $n=1.20$; $r=-0.9993$	$E=139.8$ kJ mo^{-1}; $A=11.9\cdot10^9$ s^{-1}; $n=1.21$; $r=-0.9995$
Purolite C 106 macroporous	10	H$^+$	42	5	$E=40.8$ kJ mol^{-1}; $A=98.2\cdot10^1$ s^{-1}; $n=1.34$; $r=-0.9987$	$E=992.6$ kJ mo^{-1}; $A=53.7\cdot10^5$ s^{-1}; $n=1.64$; $r=-0.9989$
		H$^+$	44	10	$E=36.6$ kJ mol^{-1}; $A=10.9\cdot10^1$ s^{-1}; $n=1.45$; $r=-0.9990$	$E=209.0$ kJ mo^{-1}; $A=10.0\cdot10^{15}$ s^{-1}; $n=1.33$; $r=-0.9995$
		Na$^+$	46	5	$E=38.4$ kJ mol^{-1}; $A=13.2\cdot10^1$ s^{-1}; $n=1.45$; $r=-0.9978$	$E=166.8$ kJ mo^{-1}; $A=60.7\cdot10^{11}$ s^{-1}; $n=1.76$; $r=-0.9994$
		Na$^+$	45	10	$E=33.4$ kJ mol^{-1}; $A=89\,1\cdot10^0$ s^{-1}; $n=1.05$; $r=-0.9994$	

[a] Cationites were of Puolite type with a granulation of 14–50 mesh

(slightly lower results) and the Flynn-Wall method (slightly higher results), as can be seen from Fig. 2.

Table 3 shows that an increase in the cross-linking from 12% DVB to >20% DVB leads to increases in the apparent kinetic parameters E, from ~59 to ~77 kJ mol^{-1} (for the first step) and ~161 kJ mol^{-1} (for the second step), and A, from ~94.10^4 to ~49.10^7 s^{-1} (in the first case) and from ~58.10^{12} s^{-1} to ~56.10^{13} s^{-1} (for the second). n has values of ~2 (for the first case) and ~1.2 (for the second dehydration process). The Na$^+$ form of the Amberlite IRC 120 cationite exhibits lower values for the apparent kinetic parameters than those for the H$^+$ form.

Effect of the granulation

The apparent kinetic parameters of the dehydraiton processes in function of the granulation are shown in Table 4.

As a rule, for all the studied cationites, increasing granulation led to increasing apparent kinetic parameter values. For example, for Vionit CC1 (8% DVB), an increase in the granulation from 60–70 mesh to 30–50 mesh resulted in E increasing from ~48 to ~63 kJ mol^{-1} (100–120°C steps) and from ~168 to ~192 kJ mol^{-1} (240–250°C step), and A increasing by ~ two orders of magnitude for the first dehydration process and from ~29.10^{13} to ~48.10^{14} s^{-1} for the second dehydration process. We assume that this might be due to a superposition of the diffusion physical process over the decomposition steps.

In addition Table 4 reveals similar effects of cross-linking on the apparent kinetic parameters to those presented in Table 3, but for a 2.5 K min^{-1} heating rate.

Effect of the heating rate

The dehydration kinetic parameters of the studied methacrylic cationites in function of the heating rate are presented in Table 5.

In most cases, a heating rate increase from 2.5 to 10 K min^{-1} caused decreases in the apparent kinetic parameters for both dehydration processes. As shown in columns 6–8, for the Purolite C104 and C106 macroporous cationites, E decreased from ~ 45 to ~36 kJ mol^{-1} for the H$^+$ form, and from ~44 to ~33 kJ mol^{-1} for the Na$^+$ form for increasing heating rate and diminishing cross-linking. It could also be observed that in most cases the values of the kinetic parameters for the Na$^+$ form were lower than those for the H$^+$ form. The apparent kinetic parameters of the Purolite cationites were affected by the cross-linking in a similar way as presented in Table 3. It should be mentioned that this variation in the apparent activation parameters might be due to a certain extent, to a compensation effect.

Conclusions

The apparent kinetic parameters n, E and A for these low-acidity methacrylic cationites in most cases exhibit lower values for the first dehydration process (located at around 100–120°C) than for the second one (240–280°C), due to the intermolecular water elimination between the proximate –COOH groups.

These parameters demonstrate the considerable effects of the experimental conditions on the thermal kinetics, due to the superposition of the physical diffusion process on the chemical dehydration processes. All of the TG curves of the studied carboxylic cationites reveal that an increase in %DVB leads to an improvement in thermal stability. Their potential use as catalysts in food technology appears possible only up to 120°C, where the first decomposition step begins.

In comparison with previous thermal studies [6] of the thermal behaviour of sulfonic polystyrene–divinylbenzene cationites, it can be concluded that carboxylic methacrylic cationites have only weak thermal stability.

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