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STUDY ON THE NON-ISOTHERMAL KINETICS OF DECOMPOSITION OF $4Na_2SO_4 \cdot 2H_2O_2 \cdot NaCl$

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The non-isothermal decomposition kinetics of $4Na_2SO_4 \cdot 2H_2O_2 \cdot NaCl$ have been investigated by simultaneous TG-DSC in nitrogen atmosphere and in air. The decomposition processes undergo a single step reaction. The multivariate nonlinear regression technique is used to distinguish kinetic model of $4Na_2SO_4 \cdot 2H_2O_2 \cdot NaCl$. Results indicate that the reaction type Cn can well describe the decomposition process, the decomposition mechanism is *n*-dimensional autocatalysis. The kinetic parameters, n, A and E are obtained via multivariate nonlinear regression. The n^{th}-order with autocatalysis model is used to simulate the thermal decomposition of $4Na_2SO_4 \cdot 2H_2O_2 \cdot NaCl$ under isothermal conditions at various temperatures. The flow rate of gas has little effect on the decomposition of $4Na_2SO_4 \cdot 2H_2O_2 \cdot NaCl$.

Keywords: *kinetics, multivariate nonlinear regression, sodium sulfate-hydrogen peroxide-sodium chloride, thermal decomposition*

Introduction

Sodium sulfate–hydrogen peroxide–sodium chloride adduct with formula $4Na_2SO_4 \cdot 2H_2O_2 \cdot NaCl$, which is also named PSC, is a known chemical entity which is useful as a peroxygen bleaching agent. The adduct can be obtained by reacting in aqueous solution, sodium sulfate, sodium chloride and hydrogen peroxide. The $4Na_2SO_4 \cdot 2H_2O_2 \cdot NaCl$ is an inclusion compound and is very stable [1, 2]. The crystalline compound has good properties as a whitener, dissolves quickly and its solubility in cold water is high. In addition, it is prepared from non-toxic starting materials that are abundant, cheap and used regularly in washing powder formulations. For a detailed description of this product, including its preparation and application in bleaching, reference is made to DE2530529 [3], GB1480884 [4], US3739312 [5], US3739313 [6], US4005182 [7], US440367 [8], JP6051611 [9], EP1258454A1 [10] and EP1258455A1 [11]. Recently, H.K. Zhao studied the phase diagram of the quaternary system $Na_2SO_4+NaCl+H_2O_2+H_2O$ [12].

Cosgrove [13] studied the thermal decomposition of $4Na_2SO_4 \cdot 2H_2O_2 \cdot NaCl$ in nitrogen atmosphere with the heating rates of 10 K min^{-1}, and a N_2 flow of 25 mL min^{-1}. Combined TG-MS was performed using a heating rate of 30 K min^{-1} and DSC was performed with an argon gas flow of 30 mL min^{-1}, and a heating rate of 10 K min^{-1}. These results indicated that the thermal decomposition of $4Na_2SO_4 \cdot 2H_2O_2 \cdot NaCl$ corresponded to obedience to the contracting circle model at first and then the Avrami-Eroveef (n=2) model. However, only one dynamic curve was given in their studies. In this paper the thermal decomposition kinetics of the adduct were carried out by using multiple dynamic TG-DSC technique. The objective of the present paper is to determine the thermal decomposition kinetics of $4Na_2SO_4 \cdot 2H_2O_2 \cdot NaCl$ in nitrogen atmosphere and in air.

Experimental

The preparation method of the $4Na_2SO_4 \cdot 2H_2O_2 \cdot NaCl$ was also described elsewhere [13]. Using laboratory grade reagents, a solution of 0.42 g NaCl in 8 g of 0.30 g mL^{-1} H_2O_2 was added dropwise to a solution of 4.09 g of Na_2SO_4 in 20 g of 0.30 g mL^{-1} H_2O_2. The resulting solution was allowed to evaporate in air and yielded well-formed crystal of $4Na_2SO_4 \cdot 2H_2O_2 \cdot NaCl$. These were ground. Analytical results show that the H_2O_2 content of the sample is 9.78%, corresponding to the two H_2O_2 per formula unit (expected 9.8%).

The experimental measurements were carried out on apparatus Netzsch STA 409PC Luxx simultaneous TG-DSC connected to a Greatwall computer under same experimental conditions, the heating rates 2.1, 4.2, 6.5 and 8.9 K min^{-1} in nitrogen atmosphere and 2.1, 4.2, 6.5, 8.9 and 11.3 K min^{-1} in air, the dynamic nitrogen or air (dry gas, 20 mL min^{-1}), the sample mass 8-10 mg. Calibration of this instrument was performed with standard indium, lead, zinc and naphthalene

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samples of known temperatures and enthalpies of melting. The metals possess over 99.99% purity and the organic compounds over 99.95%. The measured TG-DTG and TG-DSC curves are shown in Figs 1–4.

Figures 1–4 show the effect of heating rates on TG, DTG and DSC curves. It can be seen that there are same characteristics on TG-DTG and TG-DSC curves in nitrogen atmosphere and in air. The apparent decomposition temperatures become higher with increasing heating rate. The amplitude of the DSC and DTG peak decrease with heating rate decreasing. The measured TG-DSC curves further illustrate that there is an endothermic process, the whole decomposition process undergoes a single step. The slight decrease in TG curves corresponds to physical desorption of hydrogen peroxide absorbed on surface of the product of thermal decomposition of $4Na_2SO_4{\cdot}2H_2O_2{\cdot}NaCl$. The second peaks on DSC curves correspond to the transition temperature of crystal form. Analytical results indicate that the residue of thermal decomposition of the titled compound are Na_2SO_4(III) and NaCl.

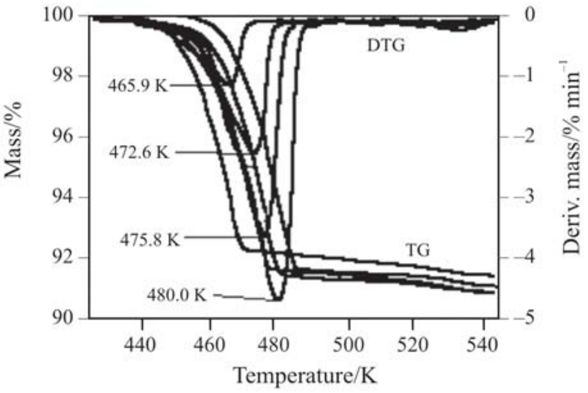

Fig. 1 Simultaneous TG-DTG curves of $4Na_2SO_4{\cdot}2H_2O_2{\cdot}NaCl$ in nitrogen atmosphere, β increasing from left to right

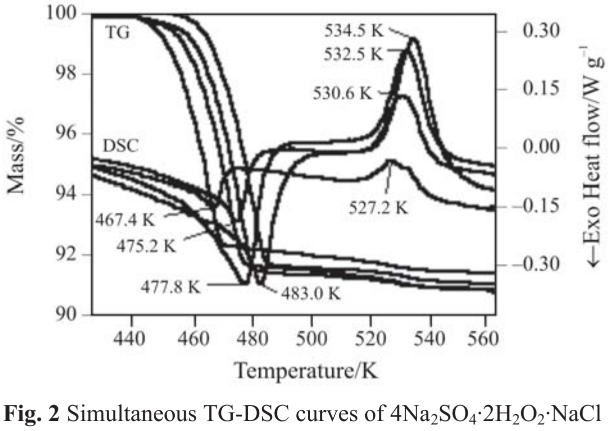

Fig. 2 Simultaneous TG-DSC curves of $4Na_2SO_4{\cdot}2H_2O_2{\cdot}NaCl$ in nitrogen atmosphere, β increasing from left to right

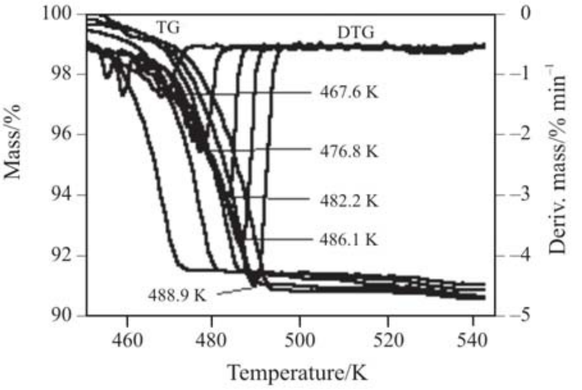

Fig. 3 Simultaneous TG-DTG curves of $4Na_2SO_4{\cdot}2H_2O_2{\cdot}NaCl$ in air, β increasing from left to right

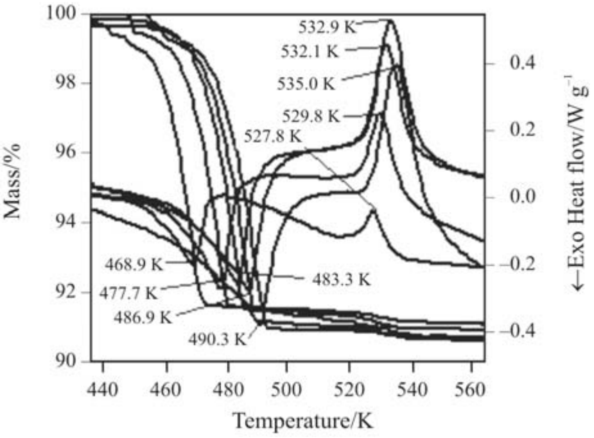

Fig. 4 Simultaneous TG-DSC curves of $4Na_2SO_4{\cdot}2H_2O_2{\cdot}NaCl$ in air, β increasing from left to right

Theoretical background

For kinetic analysis of the reaction (1) under non-isothermal conditions, Eq. (2) is generally assumed [14].

$$A(s) \rightarrow B(s) + B(g) \tag{1}$$

$$\frac{d\alpha}{dT} = \frac{1}{\beta} k f(\alpha) \tag{2}$$

where: T temperature/K, β heating rate, α mass loss, $f(\alpha)$ an expression describing the kinetic model.

The kinetic analyses are based on formal kinetic models. These models include one-, two-, or multi-step processes, in which the individual steps are linked as independent, parallel, competitive or consecutive reactions. The intermediate and final products are to be viewed as pseudo-components and may comprise a whole variety of chemical species. Arrhenius equation was used for the temperature-dependent rate constants. The following irreversible reaction type turned out to

Table 1 Reaction types and corresponding reaction equations $d\alpha/dt=A\exp(-E/RT)f(\alpha)$

Code	$f(\alpha)$	Reaction type
F1	$1-\alpha$	First-order reaction
F2	$(1-\alpha)^2$	Second-order reaction
Fn	$(1-\alpha)^n$	n^{th}-order reaction
D1	$1/2\alpha$	One-dimensional diffusion
D2	$-(1/\ln(1-\alpha))$	Two-dimensional diffusion
D3	$3(1-\alpha)^{2/3}/2[1-(1-\alpha)^{1/3}]$	Three-dimensional diffusion (Jander's type)
D4	$3/2[(1-\alpha)^{-1/3}-1]$	Three-dimensional diffusion (Ginstling-Brounstein type)
R2	$2(1-\alpha)^{1/2}$	Two-dimensional phase boundary reaction
R3	$3(1-\alpha)^{2/3}$	Three-dimensional phase boundary reaction
B1	$\alpha(1-\alpha)$	Simple Prout-Tompkins equation
Bna	$\alpha^n(1-\alpha)^n$	Expanded Prout-Tompkins equation(na)
C1–X	$(1-\alpha)(1+K_{cat.}X)$	First-order reaction with autocatalysis through the reactants, X X=a product in the complex model, frequently X=α
Cn–X	$(1-\alpha)^n(1+K_{cat.}X)$	n^{th}-order reaction with autocatalysis through the reactants, X
A2	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	Two-dimensional nucleation
A3	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	Three-dimensional nucleation
An	$n(1-\alpha)[-\ln(1-\alpha)]^{1-1/n}$	n-dimensional nucleation/nucleus growth according to Avrami-Erofeev

be applicable for the kinetic description of the decomposition of $4Na_2SO_4 \cdot 2H_2O_2 \cdot NaCl$:

$$\frac{d\alpha}{dT}=\frac{1}{\beta}k_0\exp\left(-\frac{E}{RT}\right)f(\alpha) \quad (3)$$

The $f(\alpha)$represents a function depending on the kinetic model. The $f(\alpha)$ functions corresponding to the kinetic models most commonly used in the literature are listed in Table 1 [14]. This list contains classic homogeneous reactions and typical solids reactions. In comparison to the known reaction types, the list is extended with the combined autocatalytic types C_1 and C_n, which, on careful examination, already represent parallel reactions with the same activation energy.

The kinetic parameters were fitted by running the optimization routine according to the technique of multivariate nonlinear regression, which was successfully used to determine the kinetic model for decomposition of solid [14–16]. The task of nonlinear regression is the iterative calculation of the minimum sum of least squares. In case the multivariate regression technique is applied, the total LSQ yields a sum of LSQ calculated with data from the different experimental runs

$$LSQ=\sum_{j=1}^{s}\sum_{k=l}^{N_s}\left(Y_{j,k}-\hat{Y}_{j,k}\right)^2 \quad (4)$$

The experimental values $y_{j,k}$ are the normalized mass, $y=m(T)/m_0(t=0)$ from STA. Data for all heating rates have been used simultaneously. The model values $\hat{Y}_{j,k}$ result from the numerical solution of the respective ordinary differential equations. The multivariate analysis bases on the assumption that the kinetic parameters have to be identical for all experimental conditions in the modelled parameter range. This constraint facilitates the choice of an appropriate model considerably and improves the model validity.

Results and discussion

Different models are evaluated to describe the total mass loss of the STA experiments. The material balance of the STA sample holder yields for each model, a set of ordinary differential equations. The crucible contents are described as a dynamic system with concentrated parameters. The simultaneous numerical solution of the ordinary differential equations system and the estimation of the kinetic parameters by the least squares (LSQ) method were done using Thermokinetics (Netzsch GmbH, Germany). Netzsch Thermokinetics is a software module for the evaluation of thermokinetic experiments. The differential equations are calculated using a fifth-degree Runge-Kutta embedding method with automatic optimization of the interpolation nodes for numerical solution of the reaction equations (Prince-Dormand method). To minimize the deviance of LSQ, an improved version of the hybrid procedure described in Marquardt [16] is used. This is a combination of a derivation-free, regularized Gauss-Newton procedure (Marquardt procedure) with a step-length optimization. Related details can be found in reference [17, 18]. The results of multivariate nonlinear regression on TG curves are shown in Tables 2 and 3.

Tables 2 and 3 show the multivariable nonlinear regression results. It can be seen from Tables 2 and 3 that the LSQ of CnB model is smallest and corresponds to $F_{exp}=1$. (A detailed description of the F-Test can be found in reference [18]). That is to say, the decomposition mechanism of $4Na_2SO_4 \cdot 2H_2O_2 \cdot NaCl$

Table 2 Results of nonlinear regression on TG curves for different models (in nitrogen atmosphere)

Reaction type(s)	E/kJ mol^{-1}	lg$A$	LSQ	Corr. coeff.	F_{exp}	Parameter(s)
CnB	174.84	16.91	15.69	0.99949	1.00	n=0.88567 lg$K$=0.59734
C1B	173.853	16.769	16.389	0.999457	1.043	lg$K$=0.69127
An	172.283	16.979	18.031	0.999388	1.147	n=1.54617
Fn	188.548	18.635	42.928	0.998528	2.732	n=0.14985
R2	209.57	20.77	69.494	0.99732	4.415	
A2	152.33	14.744	82.9	0.997012	5.267	
R3	220.159	21.814	95.213	0.996253	6.049	
F1	237.843	24.318	148.28	0.994058	9.421	
F2	264.202	27.295	237.97	0.990416	15.12	
A3	138.44	13.189	412.959	0.985111	26.237	
D1	323.65	33.55	424.977	0.98291	27.001	
D2	363.577	37.829	458.08	0.981245	29.104	
D4	378.9	38.924	466.551	0.980827	29.642	
D3	400.239	41.337	472.034	0.980592	29.991	
B1	138.691	14.315	1587.51	0.944101	100.862	

Table 3 Results of nonlinear regression on TG curves for different models (in air)

Reaction type(s)	E/kJ mol^{-1}	lg$A$	LSQ	Corr. coeff.	F_{exp}	Parameter(s)
CnB	152.86	14.22	21.29	0.9994	1.0	n=0.4529 lg$K$=0.5277
C1B	150.64	13.84	52.65	0.9986	2.47	lg$K$=9404
An	150.37	14.33	101.29	0.9972	4.75	n=1.7589
Fn	168.61	16.28	103.61	0.9971	4.86	n=8.03·10^{-5}
A2	144.01	13.64	125.77	0.9966	5.89	
R2	200.37	19.48	284.15	0.9921	13.31	
R3	208.94	20.26	334.43	0.9907	15.67	
F1	217.28	21.64	388.00	0.9892	18.18	
F2	224.56	22.33	446.68	0.9876	20.93	
A3	134.61	12.61	495.03	0.9863	23.19	
D3	382.71	38.55	716.19	0.9799	33.55	
D4	367.11	36.87	719.05	0.9799	33.69	
D2	354.98	36.18	727.13	0.9797	34 06	
D1	315.56	32.05	783.47	0.9781	36.70	
B1	137.08	13.98	2201.77	0.9379	103.15	

in nitrogen atmosphere and in air is all n^{th}-order with autocatalysis. But in nitrogen atmosphere, the F_{exp} values for models C1B and An are very closer to that of model CnB. The decomposition of $4Na_2SO_4\cdot 2H_2O_2\cdot NaCl$ can also be described with model An, this result is in accordance with the literature [13]. However, the case is different in air. The value F_{exp} for model An is 4.75 times of model CnB, the model An can not describe the decomposition of $4Na_2SO_4\cdot 2H_2O_2\cdot NaCl$ in air. The conclusion can be made that the reaction type CnB can well describe the decomposition of $4Na_2SO_4\cdot 2H_2O_2\cdot NaCl$ in nitrogen atmosphere and air. The decomposition mechanism of $4Na_2SO_4\cdot 2H_2O_2\cdot NaCl$ is n-dimensional autocatalysis, which can be expressed as

$$\frac{d\alpha}{dt}=k(1-\alpha)^{n}(1+K_{cat.}\alpha) \tag{5}$$

Table 4 Kinetic parameters resulting from multiple-curve analyses from TG measurement with a noise level of 0.2%

Gas	E/kJ mol^{-1}	lg$A$	n	lg$k_{cat.}$
Nitrogen	174.84	16.91	0.8857	0.5974
Air	152.86	14.22	0.4529	0.5277

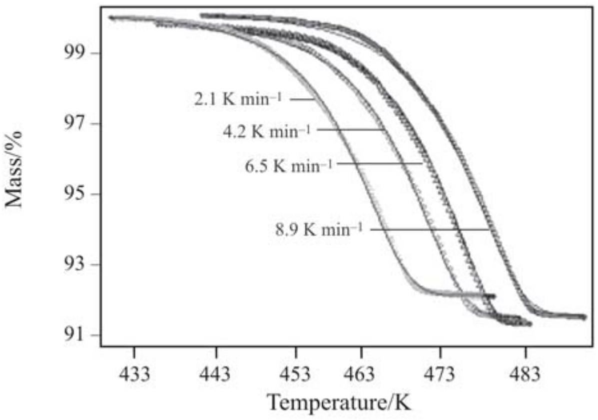

Fig. 5 Fit of TG measurements, simulated with reaction type CnB and a noise level of 0.2% for the heating rates 2.1, 4.2, 6.5 and 8.9 K min^{-1} in nitrogen atmosphere, to reaction type CnB. Signs measured, —calculated

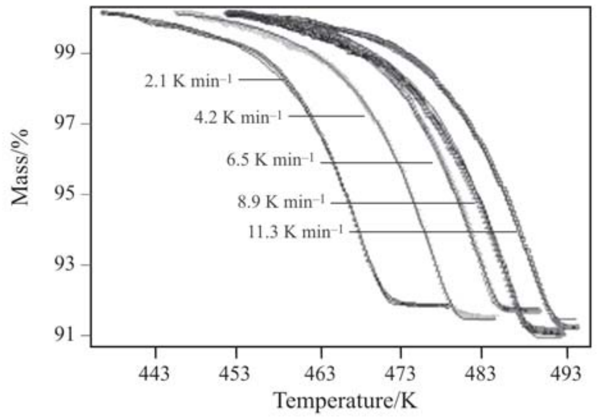

Fig. 6 Fit of TG measurements, simulated with reaction type CnB and a noise level of 0.2% for the heating rates 2.1, 4.2, 6.5, 8.9 and 11.3 K min^{-1} in air, to reaction type CnB. Signs measured, — calculated

The kinetic parameters, n, A and E are obtained via multivariate nonlinear regression, which are listed in Table 4. The decomposition processes of $4Na_2SO_4{\cdot}2H_2O_2{\cdot}NaCl$ in nitrogen atmosphere and in air are simulated (Figs 5, 6). Figures 5, 6 indicate that a satisfactory fit is possible with model CnB for the common analysis of the TG measurements.

Using these kinetic parameters obtained, the isothermal decomposition process at any temperature in nitrogen atmosphere or in air can be predicted. This procedure is done with Netzsch Thermokinetics software. The decomposition process of $4Na_2SO_4{\cdot}$ $2H_2O_2{\cdot}NaCl$ undergoes a single step reaction in nitrogen atmosphere and in air, and the mechanism is n^{th} autocatalytic. The conversion curves as a function of time with temperature as a parameter are given in Figs 7 and 8. The temperature range is from 413 to 463 K. Figures 7 and 8 show that the decomposition rate is slower in air than that in nitrogen atmosphere. For example, the decomposition process finishes in 240 min at 433 K in nitrogen atmosphere, but in air, the conversion is only 77% for 300 min at the same temperature. This is because the reaction order in nitrogen atmosphere (n=0.8857) is much greater than that in air (n=0.4529).

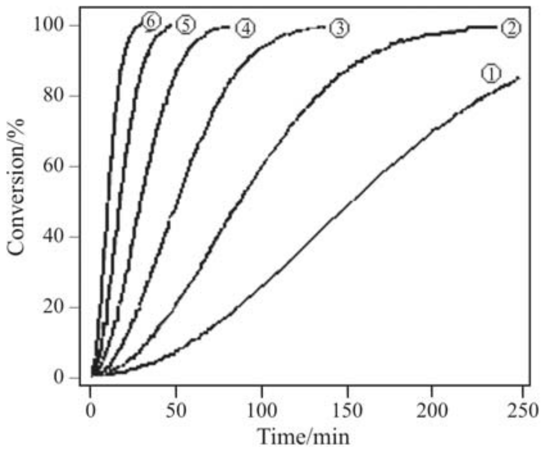

Fig. 7 Prediction of isothermal decomposition of $4Na_2SO_4{\cdot}2H_2O_2{\cdot}NaCl$ in nitrogen; 1 – 428 K, 2 – 433 K, 3 – 438 K, 4 – 443 K, 5 – 448 K, 6 – 453 K

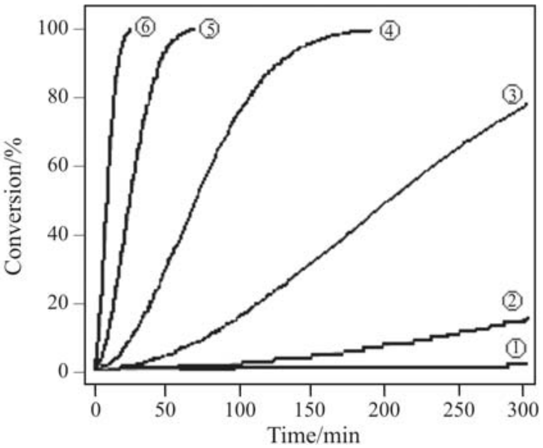

Fig. 8 Prediction of isothermal decomposition of $4Na_2SO_4{\cdot}2H_2O_2{\cdot}NaCl$ in air; 1 – 413 K, 2 – 423 K, 3 – 433 K, 4 – 443 K, 5 – 453 K, 6 – 463 K

In order to explicit the effect of gas flow rate of the decomposition of $4Na_2SO_4{\cdot}2H_2O_2{\cdot}NaCl$, further experiments were carried out at the heating rate of 8 K min^{-1} in nitrogen atmosphere. The flow rates of nitrogen are 10, 20, 30 and 50 mL min^{-1}, respectively. The simultaneous TG-DSC curves are shown in Fig. 9. It indicates that, under different flow rates, the

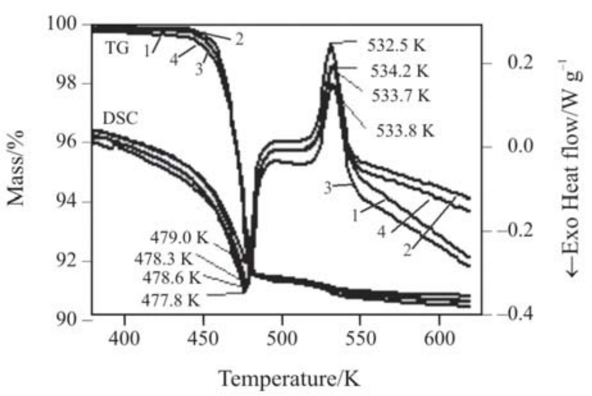

Fig. 9 Effect of flow rate of nitrogen on the decomposition of $4Na_2SO_4{\cdot}2H_2O_2{\cdot}NaCl$. The flow rates of nitrogen , 1 – 10, 2 – 20, 3 – 30 and 4 – 50 mL min^{-1}; heating rate, 8 K min^{-1}

peak temperature of decomposition of $4Na_2SO_4{\cdot}2H_2O_2{\cdot}NaCl$ are 477.8, 478.6, 478.3 and 479.0 K, respectively, the decomposition reaction of $4Na_2SO_4{\cdot}2H_2O_2{\cdot}NaCl$ start at a temperature of 440 K. Comparison with Fig. 2, the decomposition process of $4Na_2SO_4{\cdot}2H_2O_2{\cdot}NaCl$ and peak temperature are very closer under different conditions. The flow rate of nitrogen has little effect on the decomposition of $4Na_2SO_4{\cdot}2H_2O_2{\cdot}NaCl$.

Conclusions

The thermal decomposition kinetics of $4Na_2SO_4{\cdot}2H_2O_2{\cdot}NaCl$ were carried out by using multiple dynamic TG-DSC technique in nitrogen atmosphere and in air. The measured TG-DSC curves illustrate that there is an endothermic process; the whole decomposition process undergoes a single step reaction. The second peaks on DSC curves correspond to the transition temperature of crystal form. Further experiments show that the flow rate of gas has little effect on the decomposition of $4Na_2SO_4{\cdot}2H_2O_2{\cdot}NaCl$.

The multivariate nonlinear regression technique is used to distinguish kinetic model of $4Na_2SO_4{\cdot}2H_2O_2{\cdot}NaCl$. The reaction type Cn can well describe the decomposition process, the decomposition mechanism is n-dimensional autocatalysis. The results are not in accordance with that in the literature [13]. The kinetic parameters, n, A and E are obtained via multivariate nonlinear regression. Based on these kinetic parameters, the n^{th}-order with autocatalysis model is used to simulate the thermal decomposition of $4Na_2SO_4{\cdot}2H_2O_2{\cdot}NaCl$ under isothermal conditions at various temperatures. The decomposition rate is slower in air than that in nitrogen atmosphere. The reason is that the reaction order in nitrogen atmosphere (n=0.8857) is much greater than that in air (n=0.4529).

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