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AN EVALUATION ON THERMOKINETIC PARAMETERS FOR HYDROGEN PEROXIDE AT VARIOUS CONCENTRATIONS BY DSC

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Information about the kinetics and thermal decomposition of hydrogen peroxide (H_2O_2) has been required for safety reasons, due to its broad applications in many chemical industries. To determine the inherent hazards during H_2O_2 manufacturing, transportation, disposal, usage, and so on, this study deliberately selected various H_2O_2 concentrations and analyzed them by differential scanning calorimetry (DSC). In addition, thermokinetic parameters were not only established for each of these reactions, but also aimed at comprehensive, kinetic models with various tests conducted at different heating rates.

To build up a comprehensive kinetic model, various tests were conducted by heating rates of 1, 2, 4, 10°C min^{-1}, respectively. According to dynamic DSC tests, the experimental curves show that H_2O_2 decomposition has one exothermic peak and may start to decompose under 47–81°C. The total heat of decomposition is about 192–1079 J g^{-1}. Not only can these results prevent accidents caused by H_2O_2 during storage and transportation, but also assess its inherent hazards and thereby design procedures for emergency response while runaway reactions occurring.

Keywords: *DSC, H_2O_2, kinetics, runaway reactions, thermal decomposition, thermokinetic parameters*

Introduction

Historically, many process accidents have occurred worldwide. A fire-induced thermal explosion injured 21 people in Tokyo, Japan due to a tank car explosion in 1999. In 2000, an explosion injured 16 in Stratford, CT, USA; this accident cost USD 700000 dollars. Even today, thermal explosion accidents of hydrogen peroxide (H_2O_2) and its derivatives are still occurring in the world. Therefore, proactive prevention of fire and explosion hazards is the most crucial issue in process safety in Taiwan [1].

As far as the inherent hazard of H_2O_2 is concerned, its critical runaway temperature and unstable reaction criteria are still unknown. The aim of this study was to verify thermal kinetic characteristics of H_2O_2 of 10, 20, 31 and 45 mass% under runaway conditions, and to evaluate the thermal runaway data acquired from DSC [2–4]. All reaction kinetic parameters (reaction order, activation energy, frequency factor) are determined from the reaction rate–conversion–temperature relationship using logarithmic of the kinetic equation and least squares multiple linear regression of the data. However, the disadvantage of this approach is that it is applicable only to n^{th} order decompositions. Then their safety parameters can be estimated, accordingly [5, 6].

Thermal runaways can be initiated in several ways: through an uncontrollable heat of reaction, the initiation of an exothermic decomposition/oxidation, or a combination of these two [7]. It is critical that information on exothermic decomposition be easily obtainable by using small scale laboratory reactions [8–11].

Various ratio-controlled samples were used as a different marker for change in chemical composition, and hence damage assessment due to the enthalpy increased with heat rate measured and compared to those samples [12].

The physical and chemical properties of H_2O_2 have the structure of H–O–O–H, which can be dissolved in water and alcohol, but not in petroleum ether. It is the solid crystallization under the low temperature (–261–0°C). Generally speaking, it is regarded as a strong oxidant in the chemical industries [13].

Experimental

As planned, H_2O_2 containing stabilizers from MGC Pure Chemical Taiwan were tested based upon the concentrations of 10, 20, 31 and 45 mass%, respectively.

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A Mettler TA8000 system coupled with a DSC 821^e measuring cell was used for acquiring thermal curves. Any violent reaction or decomposition was performed in a high pressure crucible that can withstand about 100 bar in sealed conditions. STAR^e software was operated for acquisition of thermal curves and isothermal traces [14].

Results and discussion

This study was conducted thorough analytical experiments with simulated methods by the aid of DSC. Operating conditions, in coordination with the theories of Townsend [15] and Ishii [16], led to the results which could be used to evaluate the hazard of reactions for H_2O_2.

From experimental results, by increasing the heating rate, the reaction temperature of H_2O_2 will be advanced, and the heat that is released will be improved. Tables 1–3 show an exothermic reaction beginning at 47 and 100°C; the heat of decomposition is 192 and 1079 J g^{-1} corresponding to a heating rate of 1, 2, 4 and 10°C min^{-1}, respectively. Figures 1–4 illustrate the relationship of various concentrations of 10, 20, 31 and 45 mass% H_2O_2 corresponding to different heating rates, from which we could find different thermal curves with respect to exothermic onset temperature (T_o) and maximum temperature (T_{max}) of H_2O_2 at heating rate at 2 and 4°C min^{-1} for 10, 20, 31 and 45 mass% H_2O_2.

Figures 1–4 disclose that H_2O_2 has a higher exothermic heating rate than a low one as long as the heating rate is increased.

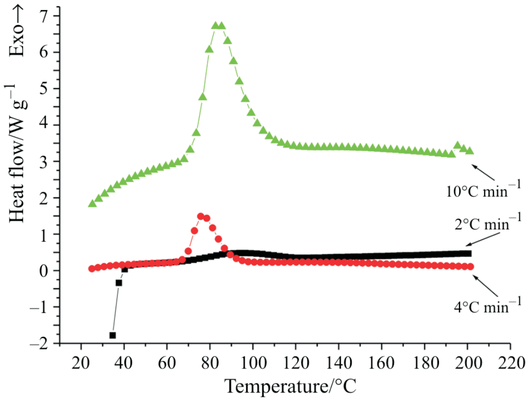

Fig. 1 DSC curves of 10 mass% H_2O_2 under dynamic scanning test

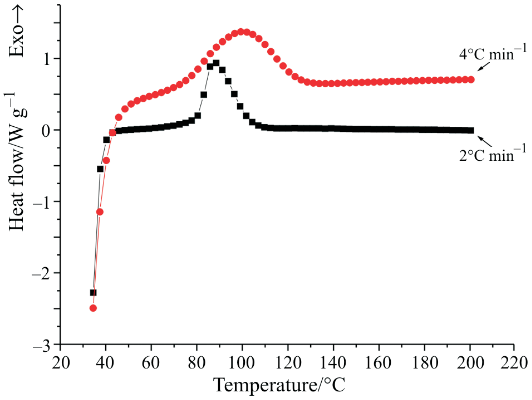

Fig. 2 DSC curves of 20 mass% H_2O_2 under dynamic scanning test

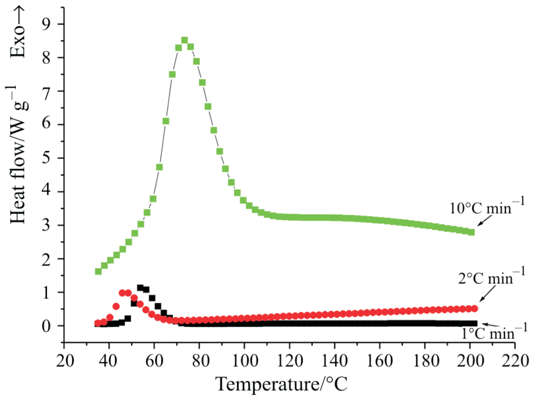

Fig. 3 DSC curves of 31 mass% H_2O_2 under dynamic scanning test

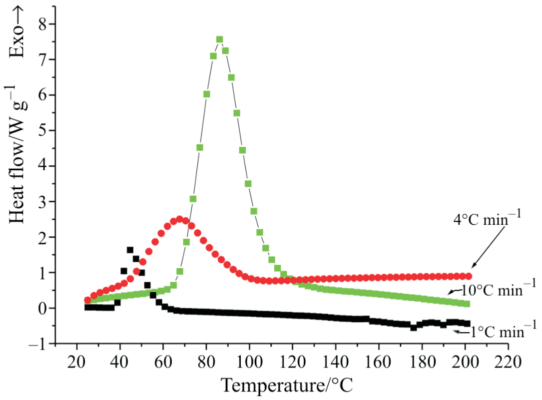

Fig. 4 DSC curves of 45 mass% H_2O_2 under dynamic scanning test

Table 1 The thermokinetic parameters from 10, 20 and 31 mass% H_2O_2 under dynamic scanning test (2°C min^{-1}) by DSC

H_2O_2/mass%	m/mg	n_1	k_0	E_a/kJ mol^{-1}	T_0/°C	T_{max}/°C	ΔH/J g^{-1}
10	2.20	1.44	27.67	102.26	52.17	92.79	192.37
20	2.20	2.57	107.37	336.97	80.48	87.67	420.97
31	2.30	2.37	90.58	256.34	40.54	46.98	703.46

Table 2 The thermokinetic parameters from 10, 20, and 45 mass% H_2O_2 under dynamic scanning test (4°C min^{-1}) by DSC

H_2O_2/mass%	m/mg	n_1	k_0	E_a/kJ mol^{-1}	T_0/°C	T_{max}/°C	ΔH/J g^{-1}
10	2.30	2.36	101.11	306.20	68.58	76.66	269.10
20	2.50	1.29	25.28	94.67	69.99	99.61	409.77
45	2.60	1.73	29.65	98.36	43.36	67.76	887.31

Table 3 The thermokinetic parameters from 10, 31 and 45 mass% H_2O_2 under dynamic scanning test (10°C min^{-1}) by DSC

H_2O_2/mass%	m/mg	n_1	k_0	E_a/kJ mol^{-1}	T_0/°C	T_{max}/°C	ΔH/J g^{-1}
10	1.50	2.84	74.64	232.18	72.87	83.79	470.64
31	1.40	2.58	53.89	166.01	57.82	73.14	838.85
45	2.30	2.13	48.48	156.54	69.05	85.80	1078.50

Due to certain uncontrollable factors, various discrepancies may arise from the experiments and simulations. To enhance the degree of accuracy in curve fitting, many methods can be employed, such as tightly sealing the measuring cell, avoiding churning in the experiment, precisely placing the materials for measurement, making frequent modifications, and so forth. By utilizing the DSC and simulated method, we could properly achieve a good degree of accuracy in curve fitting, and thereby gain accurate data for coping with any runaway reactions in real manufacturing processes.

This study used T_0 to indicate the exothermic decomposition. By evaluating the ΔH, we could use it as the degree of hazard for curtailing impact while the accident was occurring.

Conclusions

Results from DSC tests provide evidence to show that H_2O_2 is a very dangerous material. Its unstable characteristics with the –O–O– bone cause T_0 to occur earlier than other stable materials – applied in the unit of processing. This upset situation could be also controlled as temperature-reduced agents. This kind of dangerous condition of advance T_0 is the main reason in causing such serious accidents under the operating process. By using DSC, this study precisely measured the experimental data aimed at the practical concentration in a plant. All of the related hazard-information must be imbedded into the manufacturing process in order to lessen the degree of hazard under an upset situation.

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