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THERMAL DECOMPOSITION OF ORGANIC PEROXIDE WITH METALS USING CALORIMETERS

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In this study, we evaluated the reactivity of organic peroxides with metals. The effect of the metals on the decomposition of organic peroxides was measured using a differential scanning calorimeter (DSC). Results of DSC measurements showed that some organic peroxides have high reactivity with a gold plated cell. Especially, hydroperoxides were decomposed at lower temperature using the gold plated cell when compared to other type of cells.

In order to evaluate the effect of metals on the hydroperoxides, the decomposition characteristics of cumenhydroperoxide (CHP) with metal powders were studied using a C80 calorimeter and the products were analyzed by a gas chromatograph. These results indicated that the radical reaction of CHP was catalyzed by the gold and the autocatalytic reaction of CHP was catalyzed by stainless steel (SUS) and hastelloy c (HC).

Keywords: *organic peroxide, reactivity, thermal decomposition*

Introduction

Organic peroxides are generally used as initiators, hardeners and cross-linking agents. However, they are known as reactive chemicals that are decomposed by heat, mechanical shock and impurities. In addition, the heat and gas generation caused by the decomposition of organic peroxides induced many industrial accidents [1, 2]. In a chemical process, organic peroxides often come in contact with metals, such as reactors, pipes, etc. Therefore, it is important to evaluate the reactivity of organic peroxides on the metals as well as rust. For thermal analysis, various materials are used as the sample vessel. The influence of the sample vessel materials can produce different results during the thermal hazard evaluation [3].

In this study, the thermal behavior of an organic peroxide with metals was examined by several calorimeters. The influence of the sample vessel materials on the decomposition of the organic peroxides was measured by a differential scanning calorimeter (DSC). Some organic peroxides were measured in three types of sample cells, i.e., stainless steel, gold plated and glass capillary cells.

In order to investigate the influence of the sample vessels using stainless steel and gold plated materials for the thermal analysis, we studied the thermal behavior of cumenhydroperoxide (CHP) using the isothermal measurement of DSC. For the isothermal measurement, the decomposition reaction of an organic peroxide can be classified as either an n^{th} order reaction or autocatalytic reaction. In addition, the decomposition characteristics of CHP with metal powders were studied using a Calvet calorimeter (C80) and the decomposed compounds were analyzed using a gas chromatograph, ion chromatograph and gas chromatograph mass spectrometer, because the catalytic effect on the organic peroxides was discussed.

Experimental

Materials

Organic peroxides

The materials used in this study included several kinds of organic peroxides. Organic peroxides may be classified by their chemical structure. They can be classified into seven kinds of organic peroxides as follows: hydroperoxides, dialkylperoxides, peroxyesters, diacylperoxides, peroxydicarbonates, peroxy ketals and ketone peroxides. These structures are shown in Table 1. In this study, the organic peroxides with each structure were used. Table 2 lists the organic peroxides. These structures are shown in Fig. 1.

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Table 1 Classification of the organic peroxides by structure

Type	Structure
Hydroperoxides	R–O–O–H
Dialkylperoxides	R–O–O–R’
Peroxyesters	R–(C=O)–O–O–R’
Diacylperoxides	R–(C=O)–O–O–(C=O)–R
Peroxydicarbonates	R–O–(C=O)–O–O–(C=O)–O–R
Peroxy ketals	R’–C(–O–O–R)$_2$–R’’
Ketone peroxides	HO–[–O–(CRR’)–O–]$_n$–OH

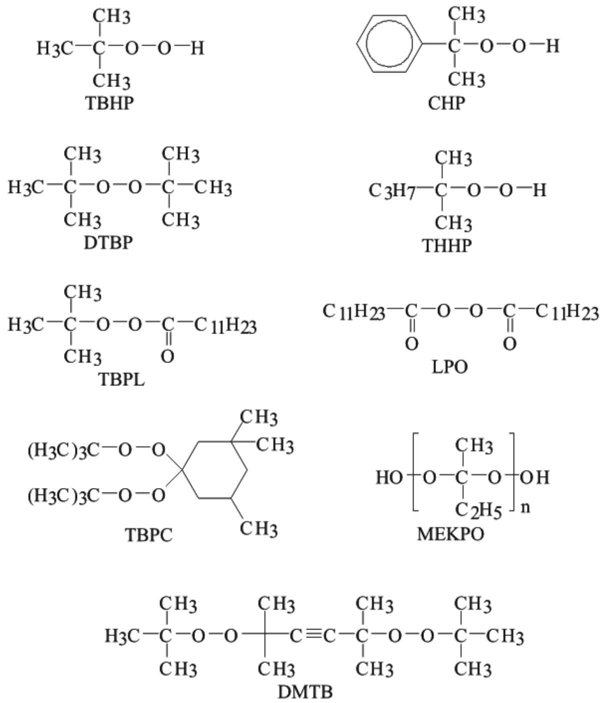

Fig. 1 The structure of organic peroxides

Metals

In order to examine the reactivity of the organic peroxide with metals, the reactivity was measured by adding metal powders, such as stainless steel (SUS304 and SUS316L), hastelloy c (HC276), gold (Au) and gold oxide (Au_2O_3). These materials were selected because they are used in chemical plants and thermal analysis. SUS and HC are used in chemical plants and as a sample vessel for thermal analysis like DSC, accelerating rate calorimeter, etc. Gold has a good stability toward chemicals. Gold is used as a sample vessel for DSC. A gold plated cell was usually used to evaluate chemicals which react with SUS. These are the chemicals like acids and halogen compounds. Gold oxide was used to compare the reactivity of gold. These were powders that had a particle size of approximately 65 μm or less.

Methods

DSC

This study of the thermal behavior of organic peroxides used the DSC (Mettler-Toledo DSC27HP). To evaluate the effect of sample cell materials, three types of high pressure sample cells were used. These were made of stainless steel (SUS303), gold plated stainless steel and glass capillary. In the experiment, nitrogen was used to purge the DSC vessel. The sample mass was approximately 2 mg. The temperature controls of DSC were used for the heat scanning and isothermal scanning program. For the heat scanning, the samples were heated from 303 to 573 K at the rate of 10 K min^{-1} and the onset temperature T_{DSC} (K) and the heat of reaction Q_{DSC} J g^{-1} were measured. For the isothermal scanning, the temperature of sample was raised at the rate of 100 K min^{-1} until reaching a predefined set temperature and then the sample was held at this temperature. The predefined temperature

Table 2 Organic peroxides used in this study

Classification by structure	Material	Purity
Hydroperoxides	*t*-Butyl hydroperoxide (TBHP)	69
	Cumen hydroperoxide (CHP)	80
	t-Hexyl hydroperoxide (THHP)	80
Dialkylperoxides	Di-*t*-butyl peroxide (DTBP)	98
	2,5-Dimethyl-2,5-*bis*(*t*-butylperoxy)hexyne-3 (DMTB)	90
Peroxyesters	*t*-Butyl peroxy laurate (TBPL)	98
Diacylperoxides	Lauroyl peroxide (LPO)	98
Peroxy ketals	1,1-*Bis*(*t*-butylperoxy)3,3,5-trimethyl cyclohexane (TBPC)	95
Ketone peroxides	Methyl ethyl ketone peroxide (MEKPO)	55

was from 398 to 418 K in 5 K increments. The induction time to the exothermic reaction and the heat of reaction were measured under isothermal conditions.

C80

The thermal behavior of the organic peroxide with metals was carried out using the C80 (Setaram). In order to evaluate the effect of the metal, the sample was placed in a pressure vessel made of stainless steel (SUS304) with an inner glass vessel. The sample mass was approximately 1 mL of CHP and a 0.1 g of the metal powder. The C80 was heated to 408 K and maintained at this temperature. After this temperature had stabilized, the sample and the reference vessels were loaded into the sensing unit of the C80. The heat of reaction Q_{C80} (J g^{-1}) and the induction time were measured by the C80.

Gas chromatograph

After the C80 experiment, the samples of the liquid product were analyzed by gas chromatograph/mass spectrometry (Shimadzu GCMS-5000). The main products detected by GC/MS were quantified by gas chromatograph (Agilent Technology GC-5890) with a flame ionization detector after the samples were diluted 5 times by toluene. The capillary column was an ULBON HR-52 (50 m, 0.25 mm i.d., Shinwa Chem. Ind.). The carrier gas, helium, was controlled at the constant flow of 1.75 mL min^{-1}.

Ion chromatograph

The samples of the liquid products included organic acids. The organic acids were quantified by ion chromatograph (Dionex DX-500). The samples were diluted from 10 to 150 times using ultrapure water. The column was a TSKgel SuperIC-AZ (150 mm, 4.8 mm i.d., Tohso). The eluent was 1.9 mmol L^{-1} $NaHCO_3$+ 3.2 mmol L^{-1} Na_2CO_3.

Results and discussion

DSC measurement

The DSC curve of the organic peroxide due to the difference in the DSC cells is shown in Figs 2 and 3. They showed the DSC curves of the exothermic peak for the organic peroxide in the glass capillary cell, SUS cell and gold plated cell. For the thermal decomposition of *t*-butyl hydroperoxide (TBHP), the DSC profiles were different between the gold plated cell and others. T_{DSC} of the gold plated cell was 358 K, for the glass capillary cell, it was 426 K and for the SUS cell, it was 415 K. T_{DSC} of the gold plated cell

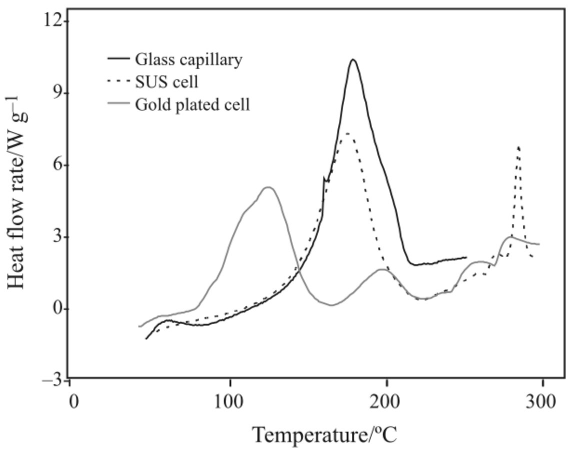

Fig. 2 Heat flow of TBHP by DSC for three types of cells

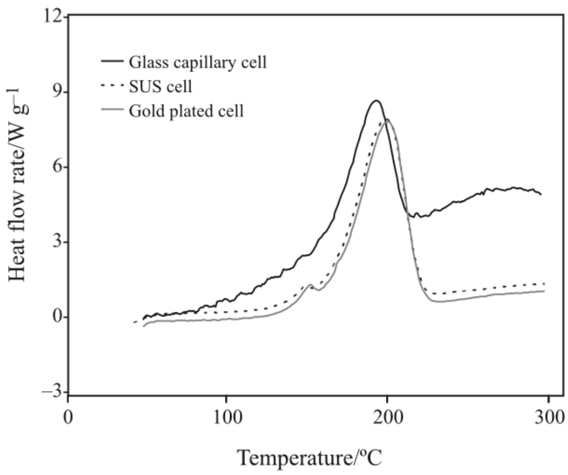

Fig. 3 Heat flow of DTBP by DSC for three types of cells

was 50 K lower than the other one. On the other hand, the sample cell materials had no effect on the decomposition of di-*t*-butyl peroxide (DTBP). T_{DSC} values of DTBP were from 434 to 439 K.

Based on the DSC measurement of the organic peroxides, some organic peroxides showed the effect of the sample cell. Table 3 shows the T_{DSC} of the organic peroxides. This reactivity was classified by the structures of the organic peroxides. The hydroperoxide group, such as TBHP, showed the significant effect of the sample cells. The dialkylperoxide group, such as DTBP and other structures showed no effect by the cells. The gold plated cell has a significant influence on the decomposition of the hydroperoxides.

The effect of gold on hydrazine hydrate has already been reported [4, 5]. Hydrazine hydrate shows a catalytic reaction by the gold. Thermal decomposition of hydrazine hydrate with metals was measured by ARC and DSC. T_{DSC} of the gold plated cell was 130 K lower than that of the glass capillary cell [5]. The gold is known as a material which has a good stability toward chemicals, but some chemical substances show

Table 3 T_{DSC} of organic peroxides by DSC measurements using three types of cells

Classification of structure	Material	Glass capillary	SUS cell	Gold plated cell
		T_{DSC}/K	T_{DSC}/K	T_{DSC}/K
Hydroperoxides	TBHP	426	415	358
	CHP	446	448	441
	THHP	442	428	373
Dialkylperoxides	DTBP	434	437	439
	DMTB	426	425	428
Peroxyesters	TBPL	407	408	409
Diacylperoxides	LPO	363	368	367
Peroxy ketals	TBPC	395	399	399
Ketone peroxides	MEKPO	393	394	383

a high reactivity. It takes notice to hazard evaluation on calorimeters.

Based on the isothermal measurement, the decomposition reaction of an organic peroxide can be classified as either an n^{th} order reaction or autocatalytic reaction. In this study, CHP was selected as a sample, because the thermal decomposition of CHP is known as an autocatalytic reaction. This reaction is caused by organic acids [6, 7]. CHP is also known as one of the hydroperoxides. In order to discuss the catalytic effect of the gold plated cell on the hydroperoxides, the thermal behavior of CHP was measured using the SUS and gold plated cells under isothermal conditions. For the isothermal measurement, the predefined temperature was set from 398 to 408 K in 5 K increments.

Figures 4 and 5 show the temperature–time curve for each holding temperature in each cell. The thermal behavior of CHP in the SUS cell showed an autocatalytic reaction. The DSC curves show a sharper profile for the heat flow rate. The maximum heat flow rate using the SUS cell was approximately 4 times that using the gold plated cell at the isothermal temperature of 408 K. The difference in both cells was more than about 20 times at 398 K. These results

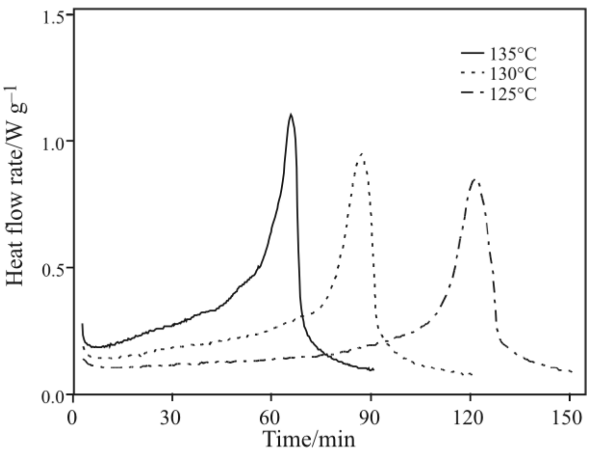

Fig. 4 Isothermal DSC curves of CHP using SUS cell

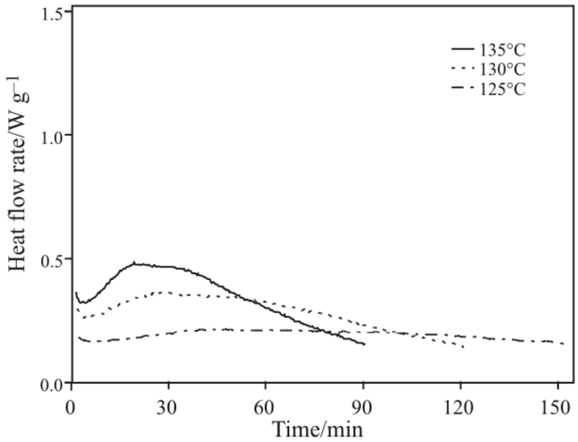

Fig. 5 Isothermal DSC curves of CHP using gold plated cell

showed that the reaction of CHP in a gold plated cell does not produce organic acids and the reaction of CHP was not autocatalytic in this cell. The catalytic effect of this cell influenced the n^{th} order reaction. Based on these results of the heat scanning and isothermal scanning DSC measurements, it can be said that the n^{th} order reaction of a hydroperoxide was catalyzed by the gold plated cell.

C80 experiment

In order to discuss the catalytic effect of gold and other metals, the thermal behavior of organic peroxides was carried out using the C80 with the inner glass vessel. CHP was used as the sample. The sample with additional metal powder was placed in the inner glass vessel. The effect of the sample vessel is canceled by the inner glass vessel. This method can evaluate the effects of additives. The holding temperature was set to 408 K.

Figures 6 and 7 show the temperature–time curve of CHP at the holding temperature. In this measurement, the decomposition of CHP was an autocatalytic

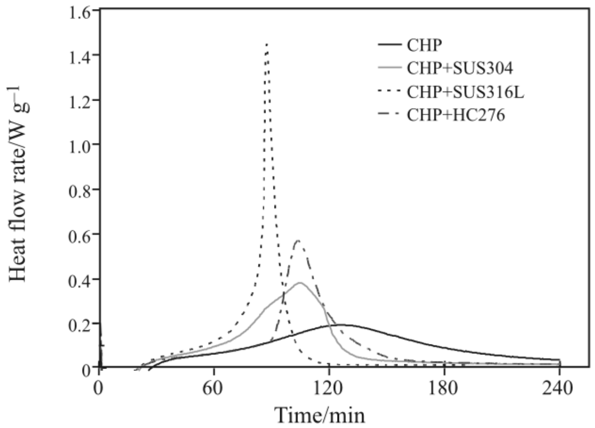

Fig. 6 Isothermal curve of CHP by C80. The isothermal temperature in 408 K

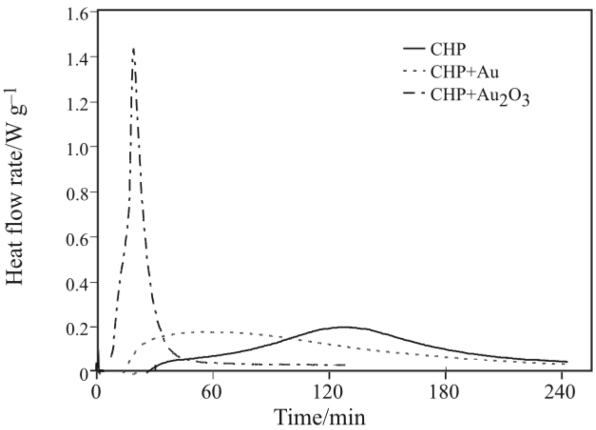

Fig. 7 Isothermal curve of CHP by C80. The isothermal temperature in 408 K

reaction, because the result of C80 showed an exothermic peak with an induction time. Comparing the result of the C80 measurement and the isothermal DSC measurement shown in Fig. 4, the maximum heat flow rate of the DSC was approximately 6 times that of C80. In the heat scanning measurement of the DSC, there was no difference in the heat flow rate between the SUS cell and glass capillary cell. In the isothermal measurement, the DSC result for the SUS cell and that of C80 with the SUS powder had a good relation. The isothermal measurement took a longer time than the heat scanning measurement, the autocatalytic activity of the sample vessel material was affected by the time of contact to the vessel.

The thermal behavior of CHP with the SUS and HC powders were an autocatalytic reaction. These temperature–time curves show a sharper profile for the heat flow rate. The maximum exothermic peak appeared after the induction time. The heat flow rate profile with the gold powder was different from the others. The reaction heat of CHP with gold powder was detected from the initial stage of the measurement. The heat flow rate of the initial stage with gold was approximately 4 times greater than without gold or with SUS and HC. The maximum heat flow rate occurred at the beginning. This reaction was an n^{th} order reaction and the catalytic activity of gold affected the radical reaction. The exothermic peak of the sample with gold oxide was more severe than the other one because the reaction was observed from room temperature. Gold is known as a stable material for organic compounds expect for ultrafine particles. However, according to the calorimetry result, gold has a catalytic effect on the decomposition of some organic peroxides.

To explain the above results, the effect of gold and other metals was investigated by chemical analysis. The reaction mechanism of organic peroxides is complex. The radical reaction induced many products. The reaction of CHP has several pathways [8]. There are radical reaction and acidolysis reaction. A typical reaction scheme is shown in Fig. 8. These main products of the radical reaction are 2-phenyl-2-propanol, acetophenone and α-methylstyrene. Acetone and phenol were the products of acidolysis [9, 10]. Organic acids were produced by the autocatalytic reaction. These main products are formic acid and acetic acid.

Table 4 shows the composition of the liquid products of CHP based on the C80 measurement. They are classified by the products. The organic acids were detected in the products of CHP without metals and with SUS and HC. The concentrations of organic acids were higher than the others. This result showed that the decomposition of CHP was an autocatalytic reaction. 2-Phenyl-2-propanol was decomposed to α-methylstyrene by the organic acids. Therefore, the concentrations of organic acids and α-methylstyrene were higher than the others.

The product of CHP with gold was converted to 2-phenyl-2-propanol and acetophenone. The concentrations of organic acids were lower than the others. A low concentration of α-methylstyrene and a large amount of 2-phenyl-2-propanol were induced by this

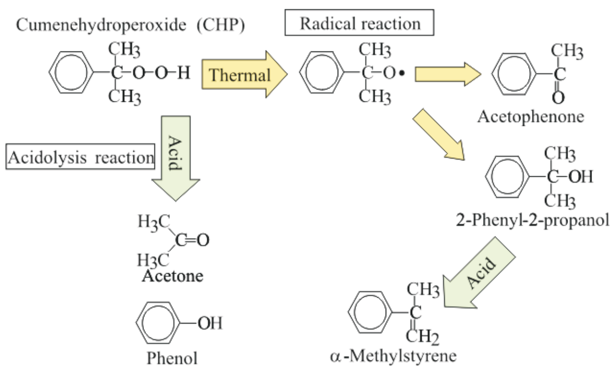

Fig. 8 Typical reaction scheme of cumenehydroperoxide

Table 4 Composition of liquid products of CHP based on C80 measurement

Products	Composition of C80 measurement/%					
	No additive	With SUS304	With SUS316L	with HC276	with Au	with Au_2O_3
Acetone	3.2	2.2	1.7	3.1	1.5	3.3
Phenol	5.0	2.0	1.5	3.6	0.7	6.9
Cumene	4.0	3.7	3.3	3.9	3.8	6.0
α-methylstyrene	3.3	3.4	4.9	5.0	1.2	14.6
Acetophenone	27.4	35.5	37.8	31.3	24.3	1.8
2-phenyl-2-propanol	28.2	21.3	23.7	23.2	51.1	34.9
Formic acid	1.9	1.4	1.2	1.6	ND	0.3
Acetic acid	0.9	0.7	0.8	0.7	0.7	0.2

effect. It can be shown that a radical reaction was induced. A different result was observed with gold oxide. The concentration of phenol and α-methylstyrene were higher than the others. The organic acids were low. It was shown that an acidolysis reaction was generated by gold oxide.

Conclusions

In order to evaluate the decomposition of organic peroxides by metals, the catalytic effect of metals on the decomposition of hydroperoxides were discussed using DSC and C80. The results of this investigation are as follows:

- According to the DSC measurements using a gold plated cell, the thermal decomposition of hydroperoxides differed from other types of cells. The T_{DSC} in the gold plated cell was lower than in a glass capillary cell and a stainless steel cell whereas there were no differences with the other structures of the organic peroxides. Gold is known as a stable material for organic compounds expect for ultrafine particles. However, gold has a catalytic effect on the decomposition of organic peroxides.
- Based on the C80 measurement and isothermal DSC measurement, the reaction of CHP showed various catalytic effects by the metals. The thermal behavior of CHP showed that SUS and HC have an autocatalytic effect on the reaction of CHP. Gold has a catalytic effect on the n^{th} order reaction of CHP.
- For the GC and IC analysis, the decomposition products of CHP were different based on the metals added to CHP. The catalytic effect of the gold for the decomposition of CHP was different from SUS or HC because the concentrations of the organic acids in the products. The autocatalytic reaction of CHP was catalyzed by SUS or HC. Gold acted as the catalyst of the n^{th} order reaction. The acidolysis reaction was catalyzed by the gold oxide.

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