Journal of Thermal Analysis and Calorimetry, Vol. 93 (2008) 1, 41–45

THERMAL HAZARD EVALUATION PROCEDURE FOR DETOXIFYING SYSTEM OF HAZARDOUS GASES BY USING OF REACTION CALORIMETER

K. Yuasa[1*], *M. Kumasaki*[2], *T. Mizutani*[2] *and M. Arai*[3]

[1]Student currently at Graduate School of Engineering, Department of Chemical System Engineering, The University of Tokyo
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan
[2]National Institute of Occupational Safety and Health, 1-4-6 Umezono, Kiyose, Tokyo 204-0024, Japan
[3]Environmental Science Center, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

The thermal behaviors of hazardous gas adsorbents were observed using a C80 calorimeter in order to develop a comprehensive thermal hazard evaluation procedure for a hazardous gas detoxifying system. Newly modified cells for the C80 were used to simultaneously monitor the pressure and the heat flow. The cells were also available for adsorbed gas switching. Adsorption/desorption experiments showed various thermal behaviors of the different gas-adsorbent combinations. The accidental incorporation of air into the cartridges proved to be a potential risk for heat generation. In addition, two kinds of experimental results in different states, static pressure and gas-circulation, were compared. As a result, the experimental apparatus used in this study exhibited the capability of evaluating the thermal hazards under the situation of accidental contamination by either air or other undesirable gases as well as normal adsorption.

Keywords: *adsorption process, C80, dry detoxifying adsorbent, hazard evaluation*

Introduction

Some hazardous gases are significantly used in semiconductor manufacturing processes as material gases. They usually exhibit flammable, explosive, corrosive, and/or toxic characteristics. Hazardous secondary gases may be produced during the reaction between the manufacturing gases, nevertheless, the industry has used them due to the market's demand. Therefore, they require special measures to avoid emission into the atmosphere.

One of the safety measures is a dry detoxifying system; an adsorbent filled in column removes and stabilizes the hazardous exhaust gases. The system is available for a wide range of gases with a suitable adsorbent and allows easily replacing saturated cartridges with new ones. Due to the advantages of the low initial cost and high detoxifying capacity, this system has been applied in many plants and laboratories.

Despite these advantages, some accidents have been reported and many thermal hazards have been recognized. In 2004, for instance, one worker was killed and two were injured by an exploding cartridge during the treating process. Previous research has been conducted from various points of view. For instance, accident investigations [1] have proposed possible scenarios and reaction mechanisms of specific gas-adsorbent combinations [2, 3]. Some manufacturers of detoxifying systems have calculated the temperature distribution inside the detoxifying column for thermal hazard assessment [4]. However, these studies have been limited to case studies, and a standard test method has not yet been suggested. Consequently, each manufacturer has individually prepared safety guidelines. This fact suggests that a comprehensive screening procedure of explosion hazards is needed for a dry detoxifying gas treating system.

In this study, the thermal behaviors of adsorbents were observed using a C80 calorimeter equipped with newly modified cells in order to develop the thermal hazard evaluation procedure for hazardous gas detoxifying system. C80 has been used to monitor thermal behaviors in absorption process [5]. Three kinds of experiments were conducted to simulate the possible situations during practical operation. The adsorption/desorption experiment includes a gas adsorption process onto an adsorbent followed by a desorption process. The adsorption process gives the amount of heat under normal condition. The difference in the desorption process *vs.* the adsorption indicates the affinity of the gas-adsorbent and adsorption feature. In this study, the adsorption/desorption heat of the NH_3-adsorbent, and CF_4-adsorbent was measured. Another experiment simulates the accidental contami-

---

[*] Author for correspondence: yuasa@explosion.chem.t-u-tokyo.ac.jp

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

nation by air. The experiment provides information about the reactivity of the gas-adsorbent *vs.* impurities. The last experiment was carried out in gas-circulation. Based on these trials, the proposed experimental apparatus has been evaluated as an appropriate apparatus for hazard evaluation procedures using a detoxifying gas treating system.

Experimental

Chemicals

As model gases to be detoxified, NH_3 (Takachiho Chemical Industrial Co., Ltd.) and CF_4 (Taiyo Nippon Sanso Co.) were used. These gases are used in semiconductor manufacturing processes. As detoxifying adsorbents, activated carbon, silica gel (Kanto Chemical. Co., Inc.), and an O_3 decomposition catalyst (Cataler Co.) were used. The activated carbon was supplied by Ajinomoto Fine-Techono. Co. Inc. Activated carbon is used for detoxifying NH_3 in industries. Other combinations of gas and absorbent are as examples to examine the hazard evaluation measure. O_2 (Taiyo Nippon Sanso Co.) was used to highlight the effect of air. O_3 (from ozonizer OP-30W, Iwasaki) was used for the gas flow experiments.

Experimental apparatus and procedure

The dry detoxifying gas treating system mainly consists of three parts; adsorption column, gas inlet, and gas outlet. Hazardous gases and inert carrier gases are introduced into the column through the inlet, and the detoxifying adsorbent filled in the column removes or stabilizes the hazardous gases. After detoxifying, the detoxified stable gases and clean carrier gases are emitted through the outlet into the atmosphere.

In this study, the thermal behaviors arising from the gas-adsorbent or impurities-adsorbent reactions were monitored by heat flow calorimeter C80 (Setaram). Two identical vessels (sample and reference cells) were used for the measurements. The vessels are capable of high pressure, gas switching and gas circulation (Fig. 1). The vessels and packing materials were each made of SUS316L and PTFE.

The experimental apparatus is shown in Fig. 2. A gas cylinder, a vacuum pump, a buffer tank and pressure gages were connected upstream of the cell. A buffer tube was connected downstream of the sample cell. The experimental procedure is as follows:

- The weighed absorbent were placed in the sample cell.
- The experimental apparatus including the reference cell was vacuated by the vacuum pump to remove impurities from the surface of the adsorbent.
- Sample gas was introduced into the cells.
- The thermal behaviors were monitored during the adsorption.
- After the adsorption attained equilibrium, the experimental apparatus was vacuated again by the vacuum pump and the thermal behaviors were monitored during the desorption (adsorption/desorption experiment). As for the contamination simulation, the experiment proceeded similar to the adsorption/desorption process until step 4. The gases were switched to the model air after the adsorption attained equilibrium. In the gas-circulation experiment, valves downstream of the sample cell were opened while the thermal behaviors were monitored.

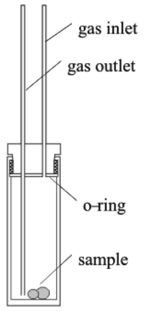

Fig. 1 The newly modified experimental vessel

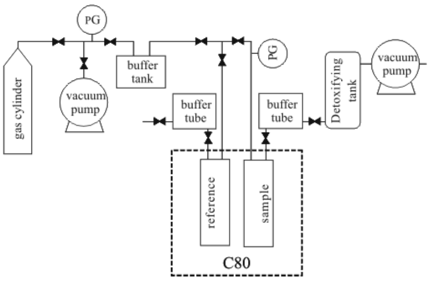

Fig. 2 Experimental apparatus

For the in adsorption/desorption experiments, activated carbon, silica gel, and the O_3 catalyst were used as the model adsorbents. NH_3 and CF_4 were applied as the sample gases to be adsorbed. Each gas was pressurized at 0.20 MPa (gage pressure). The following desorption process depressurized the experimental apparatus from 0.20 to –0.10 MPa. During an examination of the reactivity *vs.* impurities, O_2 at 0.20 MPa was added to the vessels with CF_4 at 0.10 MPa after the thermal behavior stabilized. The sample gases are circulated at around atmospheric pressure in the gas-circulation experiments. The O_3 concentration and mass flow rate were

$1.60\cdot10^{2}$ g m^{-3} and $5.2\cdot10^{-4}$ m^{3} min^{-1}. All the experiments were isothermally conducted at 313 K.

Results and discussion

Adsorption processes

The integration value of the heat flow curve, which is obtained from the C80 means the heat generated during the gas-adsorbent reaction. The heat flow curves of the NH_3-adsorbent and adsorption heat per an adsorbent mass are shown in Fig. 3 and Table 1. All the combinations of gas-adsorbents indicated exothermal behaviors. The exothermic behavior is quite reasonable taking into consideration the adsorption process.

The adsorption of gas molecules is regarded as a concentration or phase transition of chemicals on a solid surface. Gas molecules immediately gather onto fresh adsorbents after contact and fall within the influence of intermolecular forces. The condition can be regarded as a concentration of molecules, and a phase transition from the condensed phase. The phase transition attains equilibrium over time. At equilibrium, the Gibbs free energy is a minimum.

$$\Delta G = \Delta H - T\Delta S = 0 \qquad (1)$$

As the entropy of the adsorption process should be negative, the heat of adsorption, which is equal to $-\Delta H$, is essentially positive.

The experimental results indicated that each generated heat per adsorbent mass was different. The amount of heat generated should be a characteristic value of each adsorbent under the controlled pressure. This value can be utilized for hazard evaluation since the temperature rise inside the detoxifying cartridges, which is caused by the gas adsorption, may lead to the desorption or decomposition of the gases.

Desorption processes

The heat flow curves of the NH_3-adsorbent are shown in Fig. 4. The desorption heat per adsorbent mass values are shown in Table 2. All the combinations have indicated endothermic behaviors. However, the desorption heat was significantly different from the adsorption heat (absolute values) for some combinations. For example, adsorption/desorption heat of the NH_3-activated carbon are about the same values of $2.73\cdot10^{2}/-2.76\cdot10^{2}$ J g^{-1}. At the same time, that of the NH_3-silica gel are quite different of $4.15\cdot10^{2}/-2.71\cdot10^{2}$ J g^{-1}. This phenomenon explains different adsorption patterns (for example, physical adsorption and chemical adsorption) have occurred in different gas-adsorbent combinations. A physical

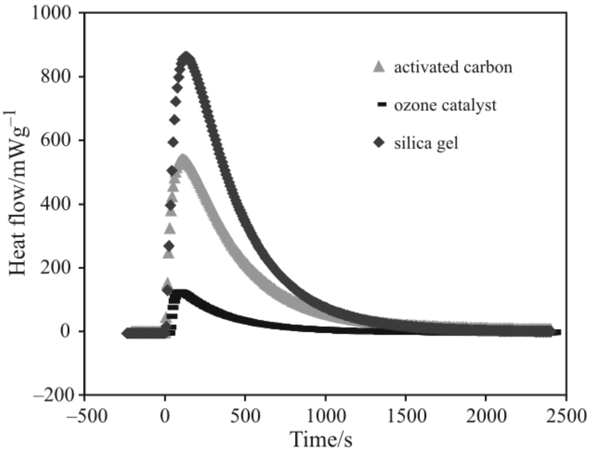

Fig. 3 Thermal behaviors of adsorption processes (NH_3)

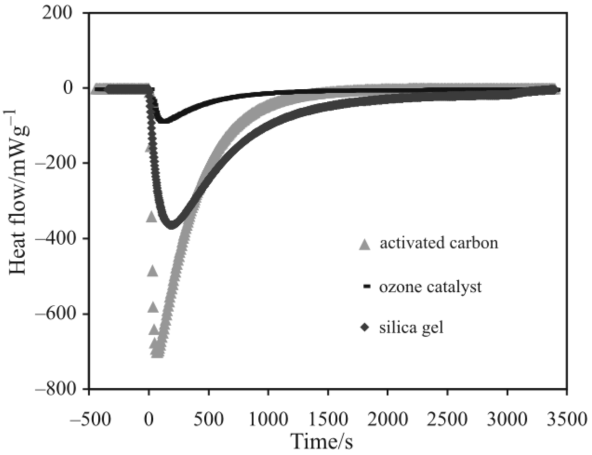

Fig. 4 Thermal behaviors of desorption processes (NH_3)

Table 1 Experimental conditions and adsorption heat per adsorbent mass

Gas	Adsorbent	Pressure/MPa	Adsorbent mass/g	Adsorption heat/J g^{-1}
NH_3	activated carbon	$2.18\cdot10^{-1}$	$3.82\cdot10^{-2}$	$2.73\cdot10^{2}$
	O_3-catalyst	$2.02\cdot10^{-1}$	$5.66\cdot10^{-2}$	$4.73\cdot10^{1}$
	silica gel	$2.00\cdot10^{-1}$	$4.48\cdot10^{-2}$	$4.15\cdot10^{2}$
CF_4	activated carbon	$2.02\cdot10^{-1}$	$2.12\cdot10^{-2}$	$4.08\cdot10^{1}$
	O_3-catalyst	$2.02\cdot10^{-1}$	$7.80\cdot10^{-2}$	$1.23\cdot10^{1}$
	silica gel	$2.00\cdot10^{-1}$	$1.73\cdot10^{-1}$	1.03

Table 2 Experimental conditions and desorption heat per adsorbent mass

Gas	Adsorbent	Pressure/MPa	Adsorbent mass/g	Desorption heat/J g^{-1}
NH_3	activated carbon	$2.18\cdot10^{-1}$	$3.82\cdot10^{-2}$	$-2.76\cdot10^{2}$
	O_3-catalyst	$2.02\cdot10^{-1}$	$5.66\cdot10^{-2}$	$-4.13\cdot10^{1}$
	silica gel	$2.00\cdot10^{-1}$	$4.48\cdot10^{-2}$	$-2.71\cdot10^{2}$
CF_4	activated carbon	$2.02\cdot10^{-1}$	$2.12\cdot10^{-2}$	$-4.15\cdot10^{1}$
	O_3-catalyst	$2.02\cdot10^{-1}$	$7.80\cdot10^{-2}$	-4.50
	silica gel	$2.00\cdot10^{-1}$	$1.73\cdot10^{-1}$	$-5.06\cdot10^{-1}$

adsorption proceeds without reactions of the adsorbent-adsorbate. Instead, the van der Waals force is the driving force for the physical adsorption. Due to this force, the adsorption and desorption process is reversible. The thermal behaviors of adsorption/desorption processes of the NH_3-activated carbon indicate a physical adsorption process.

On the other hand, if a chemical adsorption is involved in the adsorption process, the adsorption/desorption heat values are not necessarily the same. The chemical force tightly binds gas molecules and the adsorbent compared to the van der Waals force. In some combinations, gas molecules on the surface of adsorbent may be transformed through chemical reactions. The gas-adsorbent combinations which contains not only the physical adsorption but also the chemical adsorption retains gas molecules on the adsorbent to some extent even in a vacuum. The thermal behaviors differ among the different combinations. The differences in the adsorption patterns are measurable by the proposed experimental apparatus and the interaction features onto the adsorbent are provided.

Reaction with impurities

A heat flow curve is shown in Fig. 5. Both of the reactions between the adsorbent-CF_4 and adsorbent-O_2 were exothermic. The generated heat per adsorption mass was $3.77\cdot10^{1}$, 6.49 J g^{-1} for each other. This result suggests that the accidental incorporation of air into the cartridges has a potential risk to generate heat. It has become apparent that the thermal behaviors in the case of the impurity incorporation were measurable using this experimental system.

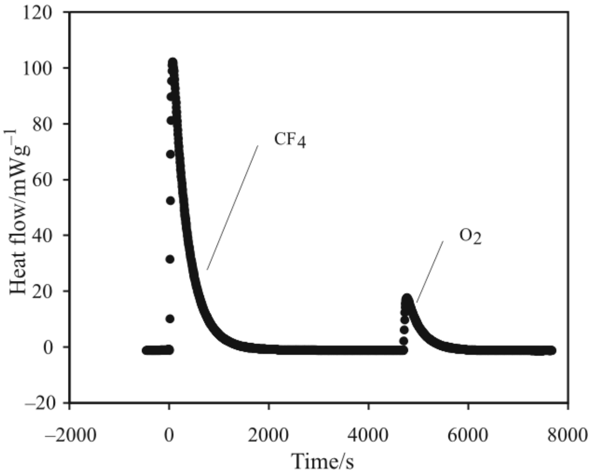

Fig. 5 Thermal behaviors of incorporation into cells (O_2)

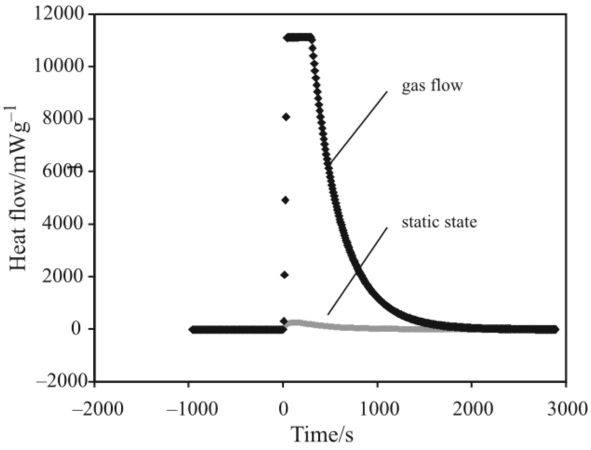

Fig. 6 Thermal behaviors of static state and gas flow

Gas flow experiments

The gas flow experiments involve a more complex process than the adsorption/desoprtion experiments. Gas molecules fall on the adsorbent accompanied by heat generation while the gas molecules are constantly supplied. On the other hand, gas flow can remove heat. Although the overall heat release behavior could be obtained by a numerical calculation or full-scale experiment, the apparatus in this study provides a small-scale and easy to handle screening test.

The heat flow curves of the O_3-activated carbon are shown in Fig. 6. Both reactions represent exothermal behaviors. However, the thermal behavior was intense in the gas-flow experiment and the heat flow curve was saturated. The generated heat per adsorbent mass in the static pressure experiment was

$1.16\cdot10^{2}$ J g^{-1}. To compare each heat generated by two different conditions, ozone inflow into sample cells were calculated. In the gas flow experiment, ozone had flowed into the cell about $1.7\cdot10^{-2}$ m^3 (calculated from the ozone concentration and gas flow period). On the other hand, in the static sate experiment, ozone inflow had been probably about the same size as the cell volume ($6.8\cdot10^{-6}$ m^3). From these calculations, ozone inflow in the gas flow experiment had been at least 2000 times larger than that of static state.

As a result of this experiment, a gas-flow adsorption sometimes generates a significant amount of heat.

Conclusions

In order to develop a comprehensive thermal hazard evaluation procedure for a hazardous gas detoxifying system, the adsorption/desorption heat of the NH_3-adsorbent, and CF_4-adsorbent was measured by a C80 calorimeter equipped with newly modified cells. The reactivity of the adsorbent with gas impurities was also examined. It became clear that the thermal behaviors of the adsorption/desorption processes and reactivity against impurities are measurable with this apparatus. In this study, the gas-flow experiment generates a significant amount of heat.

This experimental apparatus and procedure offer a small-scale and efficient hazard evaluation system to simulate abnormal detoxifying conditions as well as normal ones. The experimental values will help to quantify the hazard assessment.

References

1 M. Wakakura, Saigai no kenkyu, 26 (1992) 206.
2 A. Fukunaga, H. Itoh, Y. Mori, C. Matsumura, M. Iida, K. Tanaka and S. Kondo, Anzenkougaku Symposium 1992, pp. 19–22.
3 T. Watanabe and T. Suzuki, J. Ceram. Soc. Jpn., 105 (1997) 779.
4 Y. Aizawa and T. Nagasaka, Taiyo Nippon Sanso Technical Report, 2006, No. 25.
5 B. Gergely, A. Rédey, C. Guimon, A. Gervasini and A. Auroux, J. Therm. Anal. Cal., 56 (1999) 1233.

DOI: 10.1007/s10973-007-8777-1