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# INFLUENCE OF ATMOSPHERIC CONDITIONS ON THE SPONTANEOUS IGNITION BEHAVIOUR OF ACTIVATED CARBON

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The influence of the atmospheric conditions such as the oxygen concentration and its pressure on the spontaneous ignition behaviour of activated carbon was investigated with high pressure DSC (HP-DSC), TG-DTA and SIT (spontaneous ignition test). The onset temperature with HP-DSC lowered with the increase of the oxygen concentration and the onset temperature could be predicted with the oxygen concentration. From the adiabatic self-heating profiles observed by SIT the onset temperature lowered with the increase of the oxygen concentration and the activation energy of induction period of exothermic reaction was determined as 28~39 kJ mol$^{-1}$.

***Keywords:*** *activated carbon, oxygen concentration, spontaneous ignition*

## Introduction

Activated carbon (AC) has been widely used as adsorbents or deodorants, and known for its spontaneous ignition hazard when AC was stored with a large amount bulk. Spontaneous ignition behaviour of AC has been investigated by many scientists [1–7] and two major scenarios have been reported; physical adsorption at relatively low temperature and chemical oxidation with the oxygen in air under usual atmospheric conditions. Although a major part of the accidents reported referred the heat accumulation of exothermic oxidation of the adsorbed organic chemicals, AC with oxygen may show a self-heating followed by the ignition at relatively low temperature without any other chemicals.

It is the purpose of this investigation to obtain a better understanding of spontaneous ignition behaviour of AC high pressure DSC (HP-DSC), TG-DTA and SIT (spontaneous ignition test) were carried out. Based on the results obtained the influence of the atmospheric condition such as the oxygen concentration and the pressure on the self-heating and spontaneous ignition behaviour was discussed.

## Materials

AC used in this study was a granular Shirasagi-KL of Takeda Pharmaceutical Co. Ltd., with the diameter of 0.25 to 1.7 mm and with the loading density of 159 kg m$^{-3}$. AC was prepared by steam activation at 1200~1300 K. Physical properties of AC are shown in Table 1.

## Experimental

Pressure type DSC HP27 of Mettler-Toledo was used to investigate the influence of the oxygen concentration on the exothermic behaviour. Sample in an aluminum open cell was heated up from a room temperature to 773 K at a heating rate of 10 K min$^{-1}$ under 1, 3 and 5 MPa of various concentration of oxygen/nitrogen atmosphere such as 10/90, 21/79, 30/70 and 50/50.

Simultaneous TG-DTA system DTG-50 of Shimadzu was used to investigate the oxygen concentration of thermal behaviour of AC under 0.1 MPa of various oxygen/nitrogen atmosphere such as same as those of DSC. At first a sample was heated up from a room temperature to 403 K at a heating rate of 10 K min$^{-1}$ under 0.1 MPa nitrogen to remove the water content within the sample and was cooled down to a room temperature. Then the oxygen/nitrogen gas was introduced to the sample vessel and heated up again to 773 K at a heating rate of 10 K min$^{-1}$.

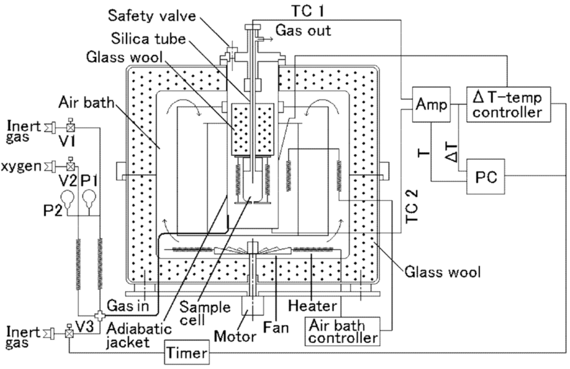

**Fig. 1** Block diagram of SIT apparatus

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**Table 1** Physical properties of AC used in this study

| Shape | Treatment | Particle diameter | Loading density | Mass loss by dry | Specific surface area | Cumulative pore volume | Average pore diameter | pH |
|---|---|---|---|---|---|---|---|---|
| granular | steam | 0.25~1.70<br>(99.8%) | 160 kg m$^{-3}$ | 4.8% | 1430 m$^2$ g$^{-1}$ | 1.1 mL/g$^{-1}$ | 3.3 nm | 6.3 |

**Table 2** Influence of the oxygen concentration and the pressure on the onset temperature of AC determined by HP-DSC

| Initial pressure/MPa | $O_2/N_2$ | | | |
|---|---|---|---|---|
| | 10/90 | 21/79 | 30/70 | 50/50 |
| 1 | 681 | 671 | 661 | 648 |
| 3 | 659 | 646 | 632 | 614 |
| 5 | 641 | 632 | 624 | 596 |

(unit: [mL g$^{-1}$])

SIT-2 for spontaneous ignition test of Shimadzu were used to investigate the self-heating behaviour under adiabatic condition under 0.1 MPa of oxygen/nitrogen atmosphere as same as those of DSC. Figure 1 shows the block diagram of SIT apparatus and a detailed description was given in [8]. In this study 343 mg of sample was loaded in the quartz cell and heated up to the desired initial temperature within nitrogen atmosphere. 180 min after the sample temperature was reached to the desired set temperature the oxygen/nitrogen gas was introduced to the sample cell with a constant flow rate and measured an adiabatic self-heating curve up to 573 K. When the sample temperature reaches 573 K the sample is judged as 'ignited' at the testing condition and the SIT stops the control and measurement, and then a nitrogen gas of room temperature is automatically introduced to the apparatus including the sample cell for safe shut down. While the sample temperature does not show any change and the temperature is kept at the initial temperature within 48 h the sample is judged as 'not ignited' and nitrogen gas is introduced to the apparatus for cooling and experiment was stopped.

## Results and discussion

### *Pressure DSC*

Figures 2–4 show the influence of the oxygen concentration on the DSC curves of AC under 1, 3 and 5 MPa atmosphere and Table 2 summarizes the DSC results. The sample mass was in a range of 2.23 to 2.63 mg. The onset temperature of AC under 1 MPa $O_2/N_2$=10/90 showed 681 K and lowered with the increase the oxygen concentration in each pressure. The lowest one was found as 596 K at under 5 MPa $O_2/N_2$=50/50. The onset temperature with the same oxygen concentration showed a good agreement, e.g. $O_2/N_2$=10/90 at 3 MPa

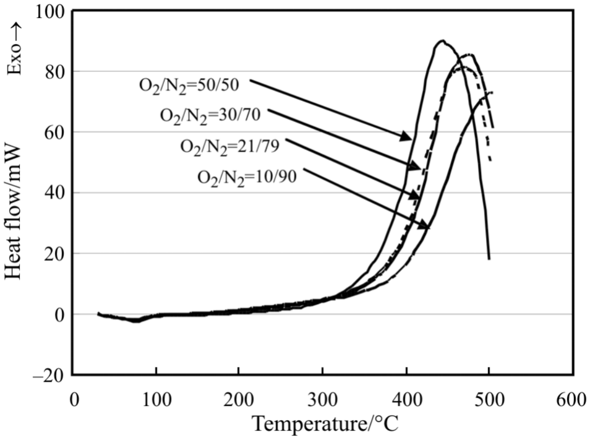

**Fig. 2** Influence of the oxygen concentration on the DSC curve of activated carbon under 1 MPa atmosphere

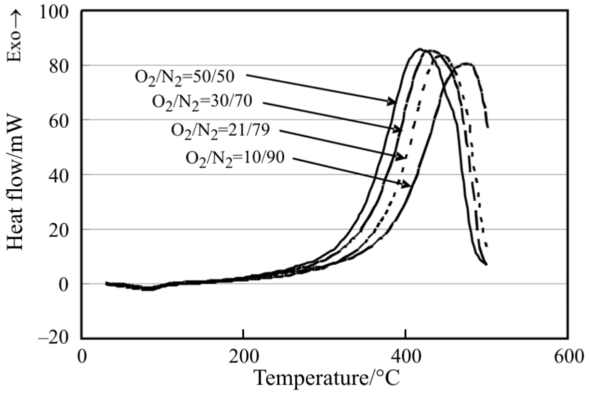

**Fig. 3** Influence of the oxygen concentration on the DSC curve of activated carbon under 3 MPa atmosphere

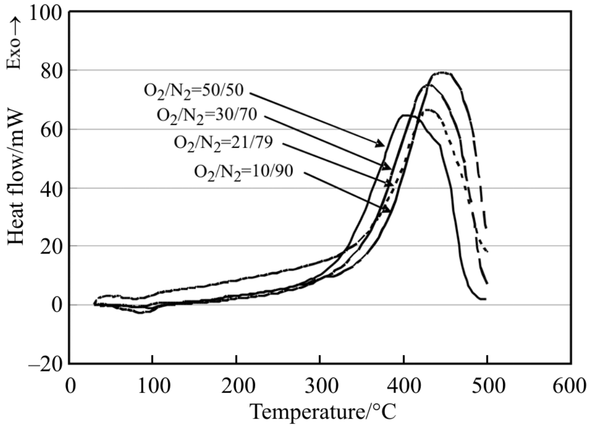

**Fig. 4** Influence of the oxygen concentration on the DSC curve of activated carbon under 5 MPa atmosphere

(659 K) and $O_2/N_2$=30/70 at 1 MPa (661 K), $O_2/N_2$=10/90 at 5 MPa (641 K) and $O_2/N_2$=50/50 at 1 MPa (648 K), $O_2/N_2$=30/70 at 5 MPa (624 K) and $O_2/N_2$=50/50 at 3 MPa (614 K). The oxygen concentration has a strong influence on the self heating behaviour of AC and the onset temperatures with the same oxygen concentration shows the same value within the experimental error.

The relation between the rate of oxygen adsorption and the temperature is expressed as follows using an Arrhenius type formula with the particle diameter and specific surface area [9];

$$r = A'(m)^{-1/3}\exp\left(-\frac{E}{RT}\right) \qquad (1)$$

$$r = A''(S)^{-1/3}\exp\left(-\frac{E}{RT}\right) \qquad (2)$$

where $r$: rate of oxygen adsorption (mL $g^{-1}$ $min^{-1}$), $m$: particle diameter (mm), $S$: specific surface area ($m^2$ $g^{-1}$) and $A'$, $A''$ constant.

Taking into account that the reaction rate is a linear function of the power function of the oxygen concentration and the power is assumed as 1/2 [9], Eq. (2) is transformed into Eq. (3);

$$r = A_0 S^{1/3} C^{1/2}\exp\left(-\frac{E}{RT}\right) \qquad (3)$$

where $C$: oxygen concentration (%), $A_0$: constant.

Eq.(4) is obtained from Eq.(3)

$$\ln\frac{1}{C^{1/2}} = -\frac{E}{R}\left(\frac{1}{T}\right) - \ln\frac{r}{A_0 S^{1/3}} \qquad (4)$$

According to Eq. (4) a plot of logarithmic oxygen concentration as a function of reciprocal onset temperature of AC is shown in Fig. 5. Each plot shows a linear relationship and it was found that the above formula could be applied to AC in this study.

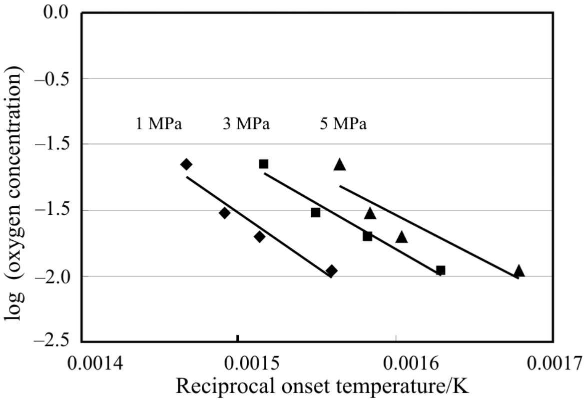

**Fig. 5** Oxygen concentration as a function of reciprocal onset temperature of activated carbon

*Simultaneous TG-DTA*

Figure 6 and Table 3 show the influence of the oxygen concentration on the TG results of AC with a heating rate of 10 K $min^{-1}$ at 0.1 MPa with a flow rate of 20 mL $min^{-1}$. The sample mass was in a range of 2.68 to 2.81 mg. Each curve shows a slight mass loss which corresponds to a vaporization of water within AC at lower than 373 K followed by a mild loss. A strong mass loss was found at around 620 K or higher. In general non-graphite type carbon has more oxidation point and is easier to be oxidized than graphite which does not show the oxidation mass loss at lower than 820 K [1]. The ratio of mass loss at 773 K increases with the increase of the oxygen concentration and 27.3% was found under $O_2/N_2$=50/50.

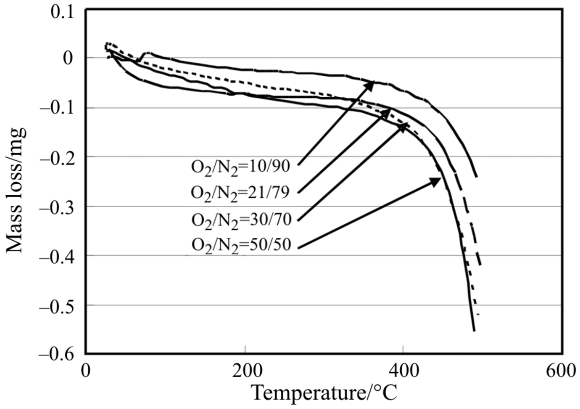

**Fig. 6** Influence of the oxygen concentration on the TG curve of activated carbon

**Table 3** Influence of the oxygen concentration on the ratio of mass loss of AC determined by TG

| $O_2/N_2$ | 10/90 | 21/79 | 30/70 | 50/50 |
|---|---|---|---|---|
| Ratio of mass loss/% | 9.84 | 16.7 | 22.1 | 27.3 |

The rate of reaction was calculated from the mass loss of TG curve and the relation between oxygen concentration and the rate of oxygen adsorption was shown in Fig. 7. As the linear relationship was obtained in Fig. 7 it was found that Eq. (4) can also be applied to TG measurement.

*Spontaneous ignition test*

As the influence of the air flow rate can not be determined with conventional microscale thermal analysis apparatus SIT has an advantage that the atmospheric flow can be controlled. As a preliminary test the air flow rate on the self-heating behaviour of AC was investigated under 0.1 MPa. Although the onset temperature with 4 mL $min^{-1}$ showed the lowest value as between

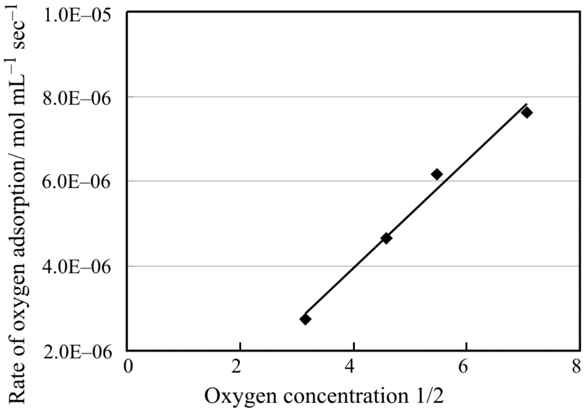

**Fig. 7** Relation between the oxygen concentration and the rate of oxygen adsorption

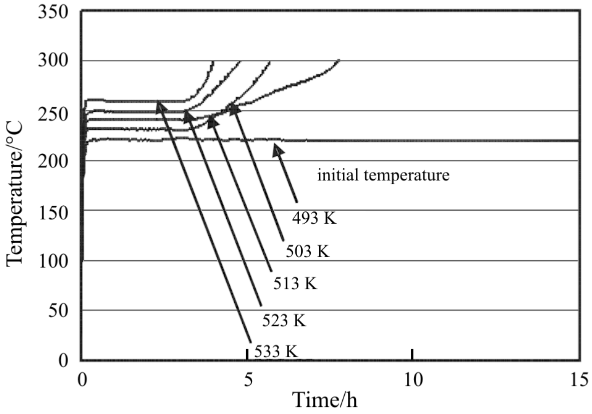

**Fig. 8** Adiabatic self-heating curves with SIT under 0.1 MPa $O_2/N_2$=10/90 atmosphere

423 and 428 K the activation energy within induction period showed a same level at 2 and 4 and that at 6 mL min$^{-1}$ showed rather high value [10]. Since the gas flow rate plays an important role on the spontaneous ignition behaviour the gas flow rate was fixed as 2 mL min$^{-1}$ in the following experiments.

Figure 8 shows the adiabatic self-heating curves of AC with SIT under 0.1 MPa $O_2/N_2$=10/90 atmosphere at a gas flow rate of 2 mL min$^{-1}$. Although no temperature rise was observed at 493 K obvious self-heating was recorded at higher than 503 K. The higher the initial set temperature is the larger the rate of temperature rise becomes. The critical temperature of self-heating was determined as between 493 K and 503 K.

Table 4 shows the SIT results of AC with the sample mass of 343 mg. The lowest self-heating temperature is defined with the 10 K stepwise. The temperature-time histories in other atmosphere showed a same tendency as $O_2/N_2$=10/90, and the lowest temperature of self-heating was observed at between 443 and 453 K for $O_2/N_2$=50/50. From the adiabatic self-heating profiles the activation energy within induction period was determined with the following formula;

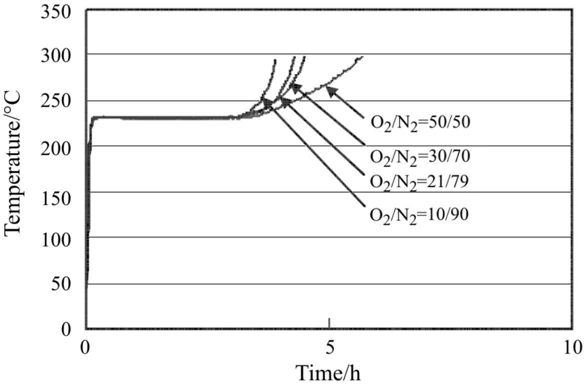

**Fig. 9** Influence of the oxygen concentration on the adiabatic self-heating curve at 503 K

**Table 4** Influence of the oxygen concentration on the SIT results of AC

| $O_2/N_2$ | 10/90 | 21/79 | 30/70 | 50/50 |
|---|---|---|---|---|
| Lowest self-heating *T*/K | 493–503 | 473–483 | 473–483 | 443–453 |
| Activation energy/ kJ mol$^{-1}$ | 28 | 38 | 39 | 38 |

$$\ln\left(\frac{dT}{dt}\right)=-\frac{E}{R}\left(\frac{1}{T}\right)+\ln\left(\frac{QA}{C_p\rho}\right) \tag{5}$$

where $Q$: heat of reaction (J mol$^{-1}$), $A$: constant (–), $C_p$: specific heat capacity (J g$^{-1}$ K$^{-1}$), ρ: density (kg m$^{-3}$).

Table 4 shows activation energies under the assumption that the reaction order was zero at an initial stage of self-heating with a slight temperature rise. The activation energy was found as about 38 kJ mol$^{-1}$ except in condition of $O_2/N_2$=10/90. This result showed an agreement with the experimental results for sawdust by Bows [1]. As, for result of $O_2/N_2$=10/90, the self-heating behaviour at lower temperature with a small reaction heat was influenced by many physical/chemical factors another factor but oxygen concentration might be dominant to lower the activation energy [11].

Figure 9 shows the adiabatic self-heating curves of AC at an initial set temperature of 503 K under 0.1 MPa of various $O_2/N_2$ atmospheres. The induction period became shorter with the increase of the oxygen concentration and the induction period for $O_2/N_2$=50/50 showed about a half of that for $O_2/N_2$=10/90. It was concluded that the oxygen concentration has a strong influence on the self-heating behaviour of AC. A detail modeling considering the heat transfer with oxygen diffusion should be the further investigation. It was found that SIT could detect the self-heating behaviour at lower than that with small scale thermal analysis it has an advantage of measurement with larger scale in adiabatic condition.

## Conclusions

From the experimental investigation of DSC, TG-DTA and SIT of activated carbon following conclusions can be drawn:

- The oxygen concentration has a strong influence on the onset temperature of AC determined with DSC and the onset temperatures with the same oxygen concentration show the same value.
- The relation between the rate of oxygen adsorption and the temperature is expressed using an Arrhenius type formula with the particle diameter and specific surface area.
- SIT could detect the self-heating behaviour at lower than that with small scale thermal analysis it has an advantage of measurement with larger scale in adiabatic condition.

## References

1 P. C. Bows, Self-heating, Elsevier, 1984.
2 A. Cameron, J. Appl. Chem. Biotech., 21 (1979) 1017.
3 K. Itoga, M. Yamada and E. Suzuki, J. Japan Soc. Safety Eng., 19 (1980) 30 (in Japanese).
4 T. X. Ren, Fuel, (1999) 1611.
5 E. Fianil, L. Perier-Cambry and G.Thomas, J. Therm. Anal. Cal., 60 (2000) 557.
6 T. Wang, R. Y. Liu, M. L. Zhu and J. S. Zhang, J. Therm. Anal. Cal., 70 (2002) 507.
7 P. L. Llewellyn and J. Rouquerol, J. Therm. Anal. Cal., 72 (2003) 1099.
8 T. Kotoyori, J. Loss Prev. Process Ind., 2 (1989) 16.
9 K. Takahashi, IHI Technical Journal, 23 (1977) 441.
10 S. Ando, Thesis, Yokohama National University, 2004 (in Japanese).
11 A. Kucuk, Y. Kadioglu and M. S. Gulaboglu, Combust. Flame, 133 (2003) 255.