THE THERMAL REGENERATION OF SPENT ACTIVATED CARBON

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Spent activated carbon loaded with methylene blue or phenol was regenerated in a nitrogen atmosphere and a steam-nitrogen atmosphere at a constant regeneration temperature. The relation between weight loss of the regenerated carbon and its adsorption capacity was investigated. Adsorption capacity was estimated by Iodine number and the decolorizing capacity of methylene blue.

In the regeneration of spent carbon in a nitrogen atmosphere, the residual material was more or less deposited on the carbon surface and the adsorption capacity of the regenerated carbon decreased.

In the regeneration of spent carbon in a steam-nitrogen atmosphere, the weight of spent activated carbon decreased with regeneration time. The weight loss rate of spent carbon was affected by the partial pressure of steam in the gas and the regeneration temperature. An empirical equation for the weight loss rate was obtained. A good correlation between Iodine number of the regenerated carbon and its weight loss was obtained.

Introduction

Recently activated carbon has been extensively used as adsorbent in municipal waste water treatment and in the removal of odors from waste gas.

Suzuki et al. investigated the regeneration of spent activated carbon loaded with many different kinds of organic materials. When volatile components such as n-hexane and butanol were adsorbed on the activated carbon, these spent activated carbons were easily regenerated under an inert gas atmosphere. However, when nonvolatile components such as phenol and methylene blue were adsorbed on the carbon, large amounts of residual material were produced in the thermal regeneration of the spent carbon under an inert gas atmosphere and adsorption capacity of the regenerated carbon became low.

Hashimoto et al. analyzed the thermal regeneration of spent activated carbon used for waste water treatment with many independent simultaneous first-order reactions which had different activation energies and showed that the thermal decomposition of adsorbed materials consisted of many complicated elemental reactions.

Kawazoe and Osawa regenerated spent activated carbon used for the waste water treatment in a helium atmosphere. A mixed gas of helium with steam under a constant rising rate of regeneration temperature and the effect of operating conditions upon the pore structure of the regenerated carbon were investigated. The pore structure of the regenerated carbon was strongly affected by the steam regeneration.

In this study, spent activated carbon loaded with phenol or methylene blue was regenerated in a nitrogen atmosphere and a steam-nitrogen atmosphere at a constant regeneration temperature. The relation between weight loss of the regenerated carbon and its adsorption capacity was investigated. Adsorption capacity was estimated by Iodine number. A good correlation between adsorption capacity of the regenerated carbon and weight loss was obtained.

1. Experimental Apparatus and Procedure

A schematic diagram of the experimental apparatus is shown in Fig. 1. Nitrogen gas from cylinder (2) was divided into two streams. One stream entered the orifice for metering the flow rate and was fed to a water bottle submerged in a constant-temperature bath. Nitrogen was saturated with steam in this bath. The flow rate of the other stream of nitrogen was measured with the orifice meter and both streams were combined and fed to the regenerator. The concentration of steam and the flow rate of feed gas to the regenerator were determined by measuring the flow rate in both streams. The regenerator used for this experiment was a stainless steel cylinder, 40 cm I.D. and 60 cm high. The spent activated carbon loaded with organic ma-
Table 1 Properties of activated carbons

<table>
<thead>
<tr>
<th>Carbon origin</th>
<th>B Petroleum pitch (Kureha beads)</th>
<th>C Coal (K-W)</th>
<th>D Coconut (G-W)</th>
<th>E Coal (X-7000)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sieve opening [mesh]</td>
<td>-20±35</td>
<td>-10±32</td>
<td>-10±32</td>
<td>-10±20</td>
</tr>
<tr>
<td>Bulk density [g/cc]</td>
<td>0.53</td>
<td>0.45</td>
<td>0.48</td>
<td>0.45-0.50</td>
</tr>
<tr>
<td>Particle density [g/cc]</td>
<td>0.90</td>
<td>0.72</td>
<td>0.82</td>
<td>0.70-0.75</td>
</tr>
<tr>
<td>Pure density [g/cc]</td>
<td>2.1</td>
<td>2.1</td>
<td>2.1</td>
<td>2.1-2.2</td>
</tr>
<tr>
<td>Surface area [m²/g]</td>
<td>1200</td>
<td>1100</td>
<td>1100</td>
<td>1120</td>
</tr>
<tr>
<td>Iodine number [mg/g]</td>
<td>1060-1180</td>
<td>1130</td>
<td>1160</td>
<td>1130</td>
</tr>
<tr>
<td>Decolorizing capacity of methylene blue [mg/g]</td>
<td>240</td>
<td>190</td>
<td>180</td>
<td>180-200</td>
</tr>
<tr>
<td>Ash weight [wt%]</td>
<td>0.5</td>
<td>6</td>
<td>1.5</td>
<td>12</td>
</tr>
</tbody>
</table>

At the start of the regenerator was heated to the regeneration temperature under constant partial pressure of steam, and then the sample basket in which the spent activated carbon was placed was put into the regenerator. The weight loss of the sample was measured continuously with the balance (13). The regeneration temperature was 400-1000°C and partial pressure of steam in the nitrogen-steam mixture was 0.0-0.21 atm. When the weight of the sample approached an adequate value, the Iodine number and decolorizing capacity of methylene blue of the regenerated carbon were measured by JIS K.1474 and JIS K.1470, respectively. The properties of activated carbons used in this experiment are shown in Table 1. Sugar, sodium dodecyl benzene sulfonate (D.B.S.), methylene blue and phenol were used as adsorbates.

Preparation of samples About 30 grams virgin activated carbon were put into 1l aqueous solution in which the organic material was dissolved to about 3000-10,000 mg/l, and the solution was stirred for 3 to 5 days. The weight of adsorbed organic material on the activated carbon was obtained from the concentration change of the solution. A Hitachi 102 spectrophotometer was used to measure the concentration of the dissolved organic material.

2. Experimental Results

2.1 Regeneration rate of spent activated carbon

Before investigating the regeneration rate of the spent activated carbon, the rate of temperature rise of the sample carbon after it was put into the regenerator was measured. The temperature of the sample carbon reached that of the regenerator within 1-2 minutes after the carbon was put into the regenerator.

When spent carbon is regenerated by a nitrogen atmosphere the weight of spent carbon decreases rapidly by the pyrolysis of organic materials on the carbon. After a few minutes its weight becomes constant. The equilibrium residual material $q_{eq}$ is defined as the residual materials per unit weight of virgin carbon when the weight of the sample becomes constant at constant temperature. When activated carbons loaded with hard-to-remove materials according to the classification of Suzuki et al.4 were regenerated in a nitrogen atmosphere, the equilibrium residual material became large. When the regeneration temperature was higher than 700°C, the equilibrium residual material was not affected by temperature. This means that the pyrolysis of the adsorbed materials on the carbon is completed below 700°C.

It is known that the adsorbate on the carbon is decomposed to CO, CO₂, H₂, CH₄ and so on by many reaction steps. When the regeneration temperature was higher than 700°C, it seemed that pyrolysis was completed in a period of a few minutes after the sample carbon was put into the regenerator.

Figure 2 shows the relationship between weight loss of the spent carbon loaded with phenol and regeneration time, with steam partial pressure as a parameter. Figure 3 shows a plot of weight loss of the spent carbon against regeneration time, with regeneration temperature as a parameter. The dotted lines in Figs. 2 and 3 are the weight of virgin carbon before adsorption.
From these figures, it is clear that the weight of spent carbon decreases rapidly in a period of a few minutes after the sample carbon is put into the regenerator, and then decreases gradually. When the spent activated carbon was regenerated for a long time under a steam-nitrogen atmosphere, the weight of spent carbon became smaller than that of virgin carbon itself under any operating conditions. It is estimated that adsorbed materials on the carbon surface are decomposed in a period of a few minutes after the carbon is put into the regenerator, followed by reaction between activated carbon itself or residual material and steam. From Figs. 2 and 3, the weight loss rate of the spent carbon becomes large when regeneration temperature and steam partial pressure are increased.

Regeneration rate of spent carbon in a steam-nitrogen mixed gas atmosphere To analyze the weight loss rate of the spent carbon the following assumptions are made.

1. Decomposition of adsorbed materials on the activated carbon is completed in a period of a few minutes after regeneration is started.
2. The weight of residual material deposited on the activated carbon after decomposition of the adsorbate is completed is almost the same weight as that of equilibrium residual material in the nitrogen atmosphere at the same regeneration temperature.

Therefore, the total weight of the sample after decomposition reaction is

$$W_R = W_S (1 + q_{eq})$$  \hfill (1)

The weight loss rate is defined as the weight loss of carbon per unit time and per unit weight of spent carbon. If the weight loss rate is a zero-order reaction with respect to carbon, the following equation is obtained from the material balance of the carbon in the regenerator.

$$- \frac{dW_T}{d\theta} = k \cdot W_T$$  \hfill (2)

Equation (2) becomes

$$- \ln(W_T/W_R) = k\theta$$  \hfill (3)

Since the weight loss of the substrate carbon in regeneration is very small, Eq. (3) becomes:

$$(W_R - W_T)/W_R = k\theta$$  \hfill (4)

**Figure 4** shows the relationship between $(W_R - W_T)/W_R$ and time $\theta$ with regeneration temperature as a parameter. From Fig. 4 the weight loss rate can be analyzed by Eq. (4). That is, the weight loss rate of the spent carbon is approximated by zero-order reaction in the steam-nitrogen atmosphere. In the regeneration of the spent carbon, Eq. (4) fitted all the data obtained from the other experimental conditions. **Figure 5** shows the relationship between $k$ and $P_{H_2O}$ with regeneration temperature as a parameter. From Fig. 5, it is clear that $k$ is proportional to $P_{H_2O}^{0.64}$. **Figure 6**
Fig. 6 Effect of $k_0$ upon regeneration temperature in steam-nitrogen atmosphere

shows the effect of regeneration temperature upon the reaction rate constant $k_0$. From Fig. 6, the activation energy of the weight loss rate in a steam-nitrogen atmosphere is found to be 36.5 kcal/mol. Hence the following empirical equation for the weight loss rate is obtained:

$$r = 1.91 \times 10^4 \exp\left(-36500/RT+273\right) \cdot P_{H_2O}^{0.64} \quad (5)$$

2.2 Gasification rate of virgin carbon

In the previous section, the empirical equation for the weight loss rate of spent carbon loaded with phenol or methylene-blue was obtained. In this section the gasification rate of the different kinds of virgin carbons is investigated for a steam-nitrogen atmosphere. Figure 7 shows the relationship between the weight of carbon $W_F$ and time $\theta$, with operating temperature as a parameter. In Fig. 7, $W_F$ decreases linearly with time and the gasification rate is shown to be independent of the kinds of virgin carbons. Figure 8 shows the relationship between $(W_F-W_T)/W_F$ and $\theta$, with operating temperature as a parameter. The solid lines in Fig. 8 were calculated from Eq. (5). In Fig. 8, the gasification rate of the virgin carbon is calculated from Eq. (5). Figure 9 compares the experimental weight loss rate with that calculated by Eq. (5). The dotted lines in Fig. 9 show 50% larger or smaller values than those calculated from Eq. (5). The experimental rate agrees with the calculated one within ±50% error regardless of the kinds of activated carbon or adsorbates. From Fig. 9, the weight loss rate of deposited residual after the pyrolysis of adsorbate is almost equal to the weight loss rate of the virgin carbon itself.

2.3 Relationship between adsorption capacity of regenerated carbon and weight loss of the carbon

Amounts of adsorption of organic compounds on
the regenerated carbon may be affected by the molecular weight and structure of adsorbates. Therefore, it is quite difficult to show what kind of standard is suitable to define the adsorption capacity of regenerated carbon. In this investigation adsorption capacity of the regenerated carbon was estimated by Iodine number. Figure 10 shows the relationship between the ratio of Iodine number of regenerated carbon to that of the virgin carbon and the regeneration temperature when the weight of spent carbon becomes equal to that of virgin carbon. From Fig. 10, Iodine number of the regenerated carbon in a steam-nitrogen atmosphere is larger than that in a nitrogen atmosphere. When the regeneration temperature is higher than 750°C, adsorption capacity is not affected by the steam partial pressure of the mixed gas. In Fig. 10, the equilibrium residual material adheres to the carbon in the case of zero steam partial pressure (nitrogen atmosphere). The relationship between \((I-I_0)/(I_{new}-I_0)\) and \(W_f/W_r\) is shown in Fig. 11. From Fig. 11, the adsorption capacity of the regenerated carbon is determined by the weight loss ratio \(W_f/W_r\) regardless of kinds of activated carbon, adsorbates or regeneration temperature. Therefore, if the weight loss of the regenerated carbon is measured, its adsorption capacity is estimated from Fig. 11.

3. Discussion

In regeneration of spent carbon in a steam-nitrogen atmosphere, not only residual material but also the carbon itself were oxidized, as shown in Figs. 2 and 3. Consequently, to regenerate spent carbon efficiently, it is very important to establish carefully the operating conditions in the regenerator. The weight loss rate of spent carbon loaded with phenol or methylene blue is expressed by Eq. (5) for a steam-nitrogen atmosphere. Equation (5) also expresses the gasification rate of different kinds of virgin carbons. This fact means that the weight loss rate of deposited residual, after pyrolysis of the adsorbate, is almost equal to the weight loss rate of the virgin carbon itself. The materials deposited on the carbon after pyrolysis of the adsorbate are carbon-rich compounds. The reaction rate of these materials with steam is of the same order of magnitude as that of the virgin carbon with steam.

Overholser and Blakely\(^3\) investigated the reaction rate of graphite at low concentration of steam. According to their result, the reaction rate was proprotional to \(P_{\text{H}_2\text{O}}\) and its activation energy was in the range of 39–59 kcal/mol. This result nearly agrees with the weight loss rate obtained by Eq. (5), that is, the reaction process of steam regeneration is an elementary reaction between carbon and steam.

Conclusion

1) The weight loss rate of spent activated carbon loaded with phenol and methylene blue is expressed by Eq. (5) for a steam-nitrogen atmosphere.

2) In this case the good correlation between the weight loss of regenerated carbon and its Iodine number was obtained in steam regeneration. Therefore, the adsorption capacity of the regenerated carbon can be estimated from its weight loss.

Nomenclature

- \(I\) = Iodine number of regenerated carbon [mg/g]
- \(I_0\) = Iodine number of spent carbon [mg/g]
- \(I_{new}\) = Iodine number of virgin carbon [mg/g]
- \(k\) = reaction rate constant of the weight loss rate of carbon [g/g-sec]
- \(k_0\) = reaction rate constant [sec\(^{-1}\cdot\text{atm}^{-0.64}\)]
- \(P_{\text{H}_2\text{O}}\) = partial pressure of steam [atm]
- \(q\) = residual material per virgin carbon [g/g virgin carbon]
This paper deals with the grinding characteristics of a target type fluid-energy mill, in which flying particles are ground by repeated impact on a target. The increase of specific surface area $AS_W$ and the distribution of particle size were investigated with respect to the following parameters: the target distance from nozzle outlet to target surface $L$, the target angle between air flow axis and target surface, the mixing ratio $m$ of particles to air by weight, and the initial air pressure.

It was found that there were optimum $L$ and $m$ values for grinding, estimated to be $70 \pm 10$ mm for $L$ and $0.7-1.0$ for $m$ over almost all the experimental range. The energy efficiency $JSW/E_f$, defined as $JSW$ per energy $E_f$ in adiabatic expansion of air, was proportional to $1.0-1.2$ power of $m$ to $m=0.7$.

On the other hand, the input energy per unit products was inversely proportional to the particle size of products in the region of fine particle size, while it was independent of the particle size of products in the region of large particle size.

Introduction

The fluid-energy mill has been increasingly used in industrial processes owing to its merits: high productivity of fine particles, small quantity of contamination during the grinding operation, suitability for heat-sensitive materials, possibility of combination with other unit operations such as drying and mixing, and simplicity of maintenance.

It has been pointed out that the efficiency of energy for grinding is very low because of the use of compressed air. In the fluid-energy mill, it has been considered that the particles accelerated by high-velocity gas are fractured by colliding with either the chamber wall or each other. However, the probability of normal particle-to-particle or particle-to-chamber wall collision is low\(^{7-9}\). For the purpose of grinding such a material, the fluid-energy mill of target type is found to be effective, because direct particle-to-target collision is certainly achieved and a large force may be produced by such an impact.

The authors have investigated the behavior of particles inside the nozzle and around various shapes of target\(^3\)-\(^4\), and they have also investigated the fracture characteristics of a single polymeric particle which collided with a target\(^5\).

The main purpose of this paper is to provide clarification of the grinding mechanism of the fluid-energy mill of target type in relation to the preceding fundamental studies\(^3\)-\(^5\).