Effect of cooling rate of KOH activation process on activated carbons

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Activated carbon was fabricated from rice husks by KOH activation. The effect of the initial cooling rate of activation on the pore structure in the activated carbon fabricated by KOH activation was investigated. The specific surface area of the activated carbon increased from 1813 to 2418 m²/g with increasing the cooling rate from 3 to 32 ºC/min. The micropore diameter in the activated carbons was distributed approximately 0.6 and 1.1 nm. The micropore volume increased from 0.86 to 1.29 cm³/g with increasing initial cooling rate. The proportion of the volume V_{micro} to the total pore volume V_{total} was calculated to be in the range from 90 to 96 %. Thus, the micropore structure of the activated carbon was strongly affected on the initial cooling rate on alkali activation.

Key words: Activated Carbon, Rice husk, Specific surface area, micro-pore, KOH activation

1. INTRODUCTION

Activated carbon is one type of commercially used adsorbent and is mainly used as a gas adsorbent [1], filter [2], catalyst [3], or electrode material [4]. Recently, many researchers have been studying the use of activated carbon for energy storage, and the hydrogen storage property of activated carbon has been reported [5]. It is important to reduce the cost of synthesizing of activated carbon and improve its performance to expand its commercial use. One way of driving down the synthesis cost is to use a waste material as the raw material. Large quantities of agricultural waste have been disposed every year. It has been reported that activated carbon can be fabricated from palm shells [6], corn cobs [7], coffee beans [8], and rice husks [9].

The pore structure of activated carbon is developed by activation. The specific surface area and adsorption property of activated carbon depend on its pore structure. The pores of porous carbon materials are classified by their diameter d into micropores (d < 2 nm), mesopores (2 < d < 50 nm), and macropores (d > 50 nm) [10]. It is known that each pores exhibit different properties and use as different applications. The activated carbon synthesized from rice husks has micropore so that it is potentially suitable for gas storage [11]. Activated carbon is fabricated from rice husks by activation with agents such as H_{3}PO_{4} [12], KOH [13], NaOH [14], K_{2}CO_{3} [15], Na_{2}CO_{3} [16] and ZnCl_{2} [17].

Activated carbon with a high specific surface area is synthesized by the alkali activation with KOH. We previously reported that activated carbon with a high specific surface area of over 2000 m²/g was fabricated from rice husks by the alkali activation with KOH [11]. This fabricated activated carbon has mainly micropore structure, giving it hydrogen storage ability at room temperature.

The adsorption performance of activated carbon basically depends on its specific surface area, and it is important to increase the specific surface area to provide adsorption performance. It is well known that the specific surface area and pore structure of activated carbon are strongly affected by the heating condition during alkali activation. The commonly considered parameters for activation are activation temperature, activation duration, heating rate, and cooling rate, as shown in Fig. 1. Among these parameters, the effect of cooling rate has not been sufficiently investigated. In this study, activated carbon was fabricated from rice husks by alkali activation with several cooling rates in an attempt to optimize the cooling rate. The effect of the cooling rate of activation on the pore structure of the activated carbon was studied.

Fig. 1. Temperature history on alkali activation.
2. EXPERIMENTAL

The activated carbon was fabricated from carbonized rice husks by alkali activation with KOH as a activation agent. The carbonized rice husks were milled and sifted using a 106 μm mesh screen. The carbonized rice husk and KOH were mixed with a KOH/raw material ratio of 5:1 by weight. The mixture was placed in a SiC crucible, heated to 850 ºC at heating rate of 8 ºC/min and then maintained at this temperature for 2h. The initial cooling rate was controlled to 3, 8, or 32 ºC/min in the temperature range from 850 to 500 ºC. The total time contained activation duration and cooling duration. Hence, the total time depended on cooling rates. The resultant activated carbon was neutralized by washing in water then dried at 120 ºC for 24 h to remove moisture.

The pore characteristics, specific surface area, pore size distribution (PSD), and pore volume were estimated by the analysis of N₂ adsorption isotherm profiles of the activated carbon samples at 77 K. The isotherm profiles were obtained by an adsorption analyzer (Belsorp-max: BEL JAPAN Co.). From the obtained isotherm profiles, the specific surface area \( S_{\text{BET}} \) and total pore volume \( V_{\text{total}} \) were calculated on the basis of the Brunauer-Emmett-Teller (BET) model [18]. The PSD of mesopore was analyzed by the Berret-Joyner-Halenda (BJH) method [19]. And the PSD of micropore was analyzed by a micropore (MP) method [20]. The micropore volume \( V_{\text{micro}} \) was calculated by the \( t \)-plot method [21].

3. RESULTS AND DISCUSSION

Figure 2 shows the N₂ adsorption isotherms at 77 K for the carbonized rice husk and the activated carbon fabricated by alkali activation with different initial cooling rates. The isotherms of the activated carbon were the Langmuir type according to the IUPAC classification [10]. The behavior of the isotherms at low relative pressure \( P/P_0 \) indicates a micropore filling phenomenon [22]. This phenomenon suggests that both of the activated carbon and carbonized rice husk has micropore structures. The low slope of the plateau in the isotherm at intermediate relative pressure \( P/P_0 \) is assigned to the adsorption of N₂ on mesopores and macropores [23]. The increase rates of the adsorption volume for the activated carbon at low and intermediate relative pressure \( P/P_0 \) were different for different initial cooling rates on alkali activation. It is suggested that the formation of meso and micropore structures were affected by the initial cooling rate. To confirm the influence of the initial cooling rate on the pore structure of activated carbon fabricated by alkali activation, \( S_{\text{BET}} \) and PSD were investigated. \( S_{\text{BET}} \) for the activated carbon was calculated by the BET model. \( S_{\text{BET}} \) for the activated carbon increased from 1813 to 2418 m²/g upon increasing the cooling rate from 3 to 32 ºC/min, as shown in Table I.

Figure 3 shows the PSD of mesopore of the carbonized rice husk and activated carbons fabricated with different cooling rates. The volume size of all pore in diameter range from 2-50 nm for activated carbon with cooling rate 8 ºC/min was larger than other activated carbons. Figure 4 shows the PSD of micropore of carbonized rice husk and the activated carbon fabricated with different cooling rates. The micropore diameter was distributed approximately 0.6 and 1.1 nm. The micropore volume \( V_{\text{micro}} \) increased from 0.77 to 1.24 cm³/g with increasing initial cooling rate as shown in Table I. These results show that the pore structure of the activated carbon was affected by the initial cooling rate on alkali activation. The ratio of \( V_{\text{micro}} \) to \( V_{\text{total}} \) was calculated by the \( t \)-plot method and ranged from 90 to 96%. The changes in the pore structure were dominated by the micropore volume. Thus, it is suggested that the micropore structure was mainly affected by the initial cooling rate.

<table>
<thead>
<tr>
<th>Cooling rate (ºC/min)</th>
<th>( S_{\text{BET}} ) (m²/g)</th>
<th>( V_{\text{total}} ) (cm³/g)</th>
<th>( V_{\text{micro}} ) (cm³/g)</th>
<th>( V_{\text{micro}}/V_{\text{total}} \times 100 (%) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>1813</td>
<td>0.86</td>
<td>0.77</td>
<td>90</td>
</tr>
<tr>
<td>8</td>
<td>1978</td>
<td>1.00</td>
<td>0.94</td>
<td>94</td>
</tr>
<tr>
<td>32</td>
<td>2418</td>
<td>1.29</td>
<td>1.24</td>
<td>96</td>
</tr>
</tbody>
</table>

Fig. 2. Nitrogen adsorption isotherms of activated carbon fabricated by KOH activation and carbonized rice husk.

Fig. 3. Pore size distributions in mesopore range of activated carbons and carbonized rice husk obtained BJH methods.

Table I. Pore properties of activated carbons.
The effect of the initial cooling rate on the micropore structure can be explained by considering the temperature of the KOH activation process. The chemical reactions involved in KOH activation progress as follows [24]:

\[
\begin{align*}
2\text{KOH} & \rightarrow \text{K}_2\text{O} + \text{H}_2\text{O} \\
\text{C} + \text{H}_2\text{O} & \rightarrow \text{H}_2 + \text{CO} \\
\text{CO} + \text{H}_2\text{O} & \rightarrow \text{H}_2 + \text{CO}_2 \\
\text{K}_2\text{O} + \text{CO}_2 & \rightarrow \text{K}_2\text{CO}_3 \\
\text{K}_2\text{O} + \text{H}_2 & \rightarrow 2\text{K} + \text{H}_2\text{O} \\
\text{K}_2\text{O} + \text{C} & \rightarrow 2\text{K} + \text{CO} \\
\text{K}_2\text{CO}_3 + \text{C} & \rightarrow 2\text{K} + 3\text{CO}
\end{align*}
\]

Chemical reaction (1) proceeds below 500 °C. Reactions (2)-(4) proceed at temperatures from 500 to 800 °C. Reactions (5)-(7) proceed above 800 °C. The micropore structure of activated carbon develops above 500 °C during KOH activation. From these expressions, reactions of (5)-(7) were occurred during alkali activation at 850 °C because activation temperature was over 800 °C. Reactions of (2)-(4) occurred at cooling process because cooling temperature was below 800 °C. The initial cooling time was investigated in the temperature range from 850 to 500 °C. Figure 5 show the temperature histories of the cooling process on KOH activation. The initial cooling times were 100, 44, and 9 min for cooling rates of 3, 8, and 38 °C/min, respectively. In addition, the ratio of $V_{\text{mic}}$ to $V_{\text{total}}$ was decreased with decreasing initial cooling rate as shown in Table I. It is indicate that mesopore or macropore volume increased with decreasing initial cooling rate. These results suggested that some micropores were coupled by reactions (2)-(5) and then coupled micropores change to mesopores or macropore. It was considered that the coupling of micropores results in destruction of micropore structure. The total time contributing to alkali activation depends on the initial cooling rate. Then, it is suggested that the effect of excess alkali activation decreased with increasing initial cooling rate. The destruction of the micropore structure is caused by excess activation, and the specific surface area and pore volume decrease with the destruction of the micropore structure.

4. CONCLUSION

The effect of the initial cooling rate of KOH activation on the microstructure of activated carbon fabricated from rice husks was investigated. The specific surface area $S_{\text{BET}}$ increased from 1813 to 2417 m$^2$/g with increasing the cooling rate from 3 to 32 °C/min.

The micropore structure of the activated carbon markedly changed with increasing cooling rate. These results show that the destruction of the micropore structure increases with decreasing cooling rate. Thus, it is suggested that the initial cooling rate affects the destruction of micropores on activated carbon fabricated by KOH activation.

REFERENCES

Effect of cooling rate of KOH activation process on activated carbons


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