Preparation and characterization of activated carbon/zeolite composites from industrial solid wastes

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Abstract

It is necessary to develop a novel method for preparing useful functional materials from the industrial solid wastes (ISWs) so as to decrease the amount of ISWs landfilled in the dump yard. The preparation of the carbon/zeolite (CZ) composites from the inorganic/organic ISWs mixture was investigated. Coal fly ash (CFA) and sawdust (SD) were used as inorganic and organic ISWs, respectively. After adding the activator (Na$_2$CO$_3$ or K$_2$CO$_3$) in aqueous solution to the mixture of CFA, SD, and bentonite as caking additive, the mixture was kneaded and extruded as a cylindrical shape. The dried green body was activated at 600 to 850°C for 1 hour in N$_2$ atmosphere. This activated cylindrical black body was hydrothermally treated in a Teflon-sealed pressure vessel with 2 mol/dm$^3$ NaOH aqueous solution at 120°C for 24 hours. The XRD patterns of the prepared composites had diffraction peaks of $P$-type zeolite together with quartz and mullite contained in the original CFA. It is found that the CZ bulk composites can be prepared by the hydrothermal alkalin treatment of the reagent-activated bulk body. The CZ composites with Na$_2$CO$_3$ prepared at 700°C had a specific surface area of 1,300 m$^2$/g-carbon and a cation-exchangeable capacity of 180 mequiv./100g-inorganic. This result indicates that the present material can remove simultaneously both non-polar and cationic contaminants from wastewater.

1 Introduction

In Japan, nearly 40 million tons of the industrial solid wastes (ISWs) are discharged every year. The total amount of these ISWs is reduced by some kinds
of intermediate treatments, and then about 5 million tons of residual ashes are landfilled in dump yards. The shortage of dump yard is one of the serious problems, because the area of level ground is very narrow in Japan. ISWs are divided into two kinds; one is inorganic wastes such as sludge and ash, and the other is the organic wastes such as plastics and biomass. The inorganic wastes have been already reused as road bed, tile and cement [1-4], but the total recycling rate is still low because of huge amount of discharged refuse. Incineration is considered as a favoured disposal method for the most organic wastes. However, the generation of dioxins and the exhaust of carbon dioxide to the environment are seriously concerned issues. Recently, a part of the organic waste begins to be used as a resource for activated carbon adsorbent [5-12], but the amount is too small to reuse all the discharged organic wastes.

The present authors have been developed an effective cascade-recycling method of the ISWs for an environmental clean-up material [13, 14]. In our method, the carbon/ceramic porous (CCP) bulk material was prepared by the calcination of cylindrical green body extruded from the kneaded mixture of sludge, sawdust, and clay mineral as caking additive in the absence/presence of an activator at 850°C under N₂ or poor oxygen atmosphere. This CCP bulk material has two adsorption properties; (1) hydrophobic adsorption ability due to the activated carbon surface originated from the sawdust and (2) ion exchange ability due to the added clay minerals. However, the inorganic ISW contained in the CCP bulk material has no adsorption ability, though it contributes to the improvement of mechanical strength of the bulk. Recently, the studies on the conversion of coal fly ash to zeolite, which is well known as a cation-exchangeable inorganic compound, have been carried out by many researchers. In this paper, we developed a technique to convert the inorganic ISW in the CCP bulk material to zeolite. Then, the characterization and absorption properties of the prepared carbon/zeolite (CZ) bulk material are described.

2 Experimentals

Coal fly ash (CFA) from coal firing power plant was used as an inorganic ISW, and sawdust (SD) was used as an organic ISW. After mixing both CFA and SD along with bentonite (B) used as caking additive (weight ratio; CFA : SD : B = 6 : 4 : 3), the mixture was kneaded with an appropriate amount of aqueous solution in the absence/presence of activator (Na₂CO₃ or K₂CO₃). The kneaded one was extruded as a cylindrical shape. Then, the wet green body was dried at 50°C for 3 days and activated at 600, 700, or 850°C for 1 hour under N₂ atmosphere. The calcined black body was hydrothermally treated in Teflon-sealed pressure vessel with 2 mol/dm³ NaOH aqueous solution at 120°C for 20 hours. The prepared CZ bulk material was rinsed with deionized water for several times and dried at 50°C. The abbreviation of CZ bulk materials with/without activator is listed in Table 1.

The crystalline phase in the CZ bulk material was identified by X-ray diffractometry (XRD). The microstructure of the cross section was observed by the scanning-electron microscopy (SEM). The specific surface area (SSA) was
estimated by BET method using N₂ gas. The cation-exchangeable capacity (CEC) was evaluated by the calcium-conversion method. The adsorption ability of CZ bulk materials was characterized by the adsorption of methylene blue (MB) from aqueous solution. The measurement procedure of MB adsorption is implemented according to the Japan Industrial Standard (JIS).

Table 1: Abbreviated sample names.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>CZ0</th>
<th>CZN</th>
<th>CZK</th>
</tr>
</thead>
<tbody>
<tr>
<td>activator</td>
<td>none</td>
<td>Na₂CO₃</td>
<td>K₂CO₃</td>
</tr>
</tbody>
</table>

Figure 1: XRD patterns of CFA (a) and CZ0 calcined at 600 (b), 700 (c) and 850 (d) °C. ◎: quartz, +: mullite, ●: Na-P type zeolite.

3 Results and discussion

3.1 CZ0 bulk materials

Figure 1 shows XRD patterns of CFA and CZ0 materials prepared at different calcination temperature. After the calcination and hydrothermal treatment, diffraction peaks of the Na-P type zeolite were observed in all the CZ0 bulk materials, while the diffraction intensities of quartz and mullite decreased. The result shows that Na-P type zeolite forms through the dissolution and precipitation of Si and Al species by alkali-hydrothermal treatment. Therefore, it is possible to synthesize Na-P type zeolite and hybridize it with carbon adsorbent by alkali-hydrothermal treatment. The CEC and SSA values of the obtained CZ0 bulk materials are shown in Table 2. CEC value increased with an increase in the calcination temperature. The oxide species containing Si and/or Al formed at higher calcinations temperatures will dissolve easily into NaOH aqueous solution, which leads to an increase in the amount of synthesized zeolite, hence
an increase in the CEC values. The SSA value of CZ0 bulk at 700°C had a maximum value, which depends on the activated degree of carbonized SD surface. Therefore, it is concluded that the optimum calcination temperature is 700°C for effective activation in the present CZ0 bulk material.

Table 2: CEC and SSA values of CZ0 bulk materials.

<table>
<thead>
<tr>
<th>temperature (°C)</th>
<th>CEC (meq./100g)</th>
<th>SSA (m²/g-carbon)</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>192</td>
<td>636</td>
</tr>
<tr>
<td>700</td>
<td>230</td>
<td>791</td>
</tr>
<tr>
<td>850</td>
<td>244</td>
<td>731</td>
</tr>
</tbody>
</table>

a) Weight of carbon contained in CZ0 bulk material

3.2 CZN bulk materials

XRD patterns of the bulk body with Na₂CO₃ activator calcined at different temperatures are shown in Figure 2. Though the XRD pattern did not change before and after calcination in the absence of activator, the crystalline phases formed changed in the presence of Na₂CO₃ activator. The diffraction peaks of crystalline NaAlSiO₄ were observed in the samples calcined at 600 and 700°C. Furthermore, the sample calcined at 850°C showed the diffraction peaks originated from crystalline nepheline. These minerals might be produced by the solid state reaction among Na₂CO₃, quartz, mullite, amorphous components in CFA and clay, because the diffraction intensities of quartz, mullite and amorphous hallow decreased. Weight loss of calcined samples with Na₂CO₃ was 27-30 wt%, which was larger than the weight loss of calcined sample without activator (23-25 wt%). This result suggests that the reagent Na₂CO₃ activated the surface of carbonized SD.

![XRD patterns](image)

Figure 2: XRD patterns of the bulk body with Na₂CO₃ activator calcined at (a) 600, (b) 700, (c) 850°C. ◎: quartz, ＋: mullite, ◊: NaAlSiO₄, ◀: nepheline.
Figure 3: XRD patterns of CZN materials obtained at calcination temperatures of (a) 600, (b) 700, and (c) 850°C. ◎: quartz, ◦: mullite, ○: nepheline, ●: Na-P type zeolite, ▲: faujasite.

XRD patterns of CZN bulk materials prepared by the hydrothermal treatment at 120°C for 20 hours in 2.0 mol/dm³ NaOH aqueous solution are shown in Figure 3. In the case of CZ bulk materials, the only Na-P type zeolite formed by alkali-hydrothermal treatment, but two types of zeolite such as Na-P type and faujasite type were prepared in the CZN bulk material. It is well known that the faujasite type zeolite possesses larger sized pores than those of Na-P type zeolite. Therefore, the formation of faujasite is favourable for removal of toxic organic cations from wastewater than Na-P type zeolite. It is noticed by comparison of the peak intensities of CZN samples obtained at different temperatures, that faujasite type zeolite will be formed at lower temperatures. In XRD profile of CZN sample calcined at 850°C, the nepheline minerals remained after hydrothermal synthesis. The calcination at higher temperatures is known to accelerate the activation of carbonized SD surface in the case of reagent activation. However, excess preheating at high temperature encourages the production of more stable minerals, so that the optimal preheating temperature to prepare the activated carbon/zeolite composites is less than 700°C.

The CEC and SSA values of CZN bulk materials are shown in Table 3. The SSA values of CZN samples were considerably larger than that of CZ0 and CZN samples before the alkali-hydrothermal treatment. However, CEC values of CZN samples exhibited smaller values than that of CZ0 samples which contain the Na-P type zeolite. The decrease in CEC values seems to be caused by the reduction of the amount of zeolite phases formed. Therefore, the increase of SSA values would be responsible for the removal of activator during the alkali-hydrothermal treatment, but not caused by the production of Na-P type and/or faujasite type zeolites. Figure 4 shows the MB isothermal adsorption equilibrium curves of CZN materials before and after the hydrothermal treatment. MB adsorption ability was improved by the alkali-hydrothermal
treatment. This is caused by the conversion of the inorganic compounds included in the preheated black body into zeolite with high cation-exchangeable ability. CZN samples preheated at 850°C exhibited lower adsorption ability than other samples. This verifies that the amount of zeolite formed is decreased on account of the formation of nepheline minerals in the preheating process. Though the CEC performance degraded by adding Na$_2$CO$_3$ activator, CZN bulk materials possessed very large SSA per carbon weight. Therefore, this material has a potential to be used as an environmental clean-up material, which can adsorb both various kinds of cationic compounds and organic compounds with poor polarity.

<table>
<thead>
<tr>
<th>temperature (°C)</th>
<th>CEC (meq./100g)</th>
<th>SSA (m$^2$/g-carbon$^a$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>158</td>
<td>1725(50$^b$)</td>
</tr>
<tr>
<td>700</td>
<td>158</td>
<td>1299(44$^b$)</td>
</tr>
<tr>
<td>850</td>
<td>131</td>
<td>990(395$^b$)</td>
</tr>
</tbody>
</table>

a) Weight of carbon contained in CZN bulk material
b) SSA values before hydrothermal treatment

Figure 4: MB adsorption equilibrium curves of CZN samples before (filled) and after (open) hydrothermal treatment. 600 (squares), 700 (circles), and 850 (triangles)°C.

3.3 CZK bulk materials

Figure 5 shows the XRD patterns of the calcined black body with K$_2$CO$_3$ activator. The diffraction intensities for the original CFA decreased after the calcinations at 600°C. The formation of crystalline KAISiO$_4$ was confirmed with an increase in the preheating temperature. The KAISiO$_4$ mineral will be formed by the solid state reaction among K$_2$CO$_3$, quartz and mullite. Carbon content of
the sample calcined at 850°C decreased from ca. 11 wt% to ca. 7 wt%, which suggested that carbonized SD can be activated by K₂CO₃ activator.

XRD patterns of CZK materials calcined at different temperatures are shown in Figure 6. In the CZK samples preheated at 600 and 700°C, Na-P type zeolite, which was also observed in CZN samples, could be identified. However, the diffraction peaks of this zeolite are slightly broadened, which shows that phillipsite will be formed. On the other hand, the diffraction peaks originated from analcime, which is a kind of zeolite materials with small pore size (ca. 0.3 nm), can be observed in XRD pattern of the CZK sample calcined at 850°C. The analcime formation will be cased by the KAlSiO₄ obtained by calcination at 850°C.

Table 4: CEC and SSA values of CZK bulk materials.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>CEC (meq./100g)</th>
<th>SSA (m²/g-carbon)</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>148</td>
<td>471(54b)</td>
</tr>
<tr>
<td>700</td>
<td>168</td>
<td>833(212b)</td>
</tr>
<tr>
<td>850</td>
<td>85</td>
<td>881(584b)</td>
</tr>
</tbody>
</table>

a) Weight of carbon contained in CZK bulk material
b) SSA values before hydrothermal treatment

Figure 5: XRD patterns of the black body with K₂CO₃ activator calcined at (a) 600, (b) 700, and (c) 850°C.◎: quartz, +: mullite, □: KAlSiO₄.

Table 4 shows the CEC and SSA values of CZK bulk materials. The CEC value of CZK material has a maximum value at the calcinations temperature of 700°C. The degradation of CEC values attributes to the formation of analcime. Thus, the calcinations temperature for preparing high CEC bulk material is optimal at 700°C in the case of K₂CO₃ activator. Moreover, the SSA value of the CZK material at 700°C was largest.

To clarify the adsorption ability of the CZK bulk material prepared under the optimal condition, the MB adsorption of CZK materials was investigated, as
summarized in Figure 7. The MB adsorption ability of the CZK samples before calcination increased with an increase in the calcination temperature. The SSA values of these samples also increased with increasing calcinations temperature. Thus, the high adsorption ability can be explained by an increase of the SSA value, \textit{i.e.}, by an increased activation at higher temperatures. The adsorption ability of all CZK materials increased due to the alkali-hydrothermal treatment. The formation of cation-exchangeable zeolite is responsible for this increase in the MB adsorption ability. The degradation of MB adsorption ability at 850°C will be caused by the analcime formation. These results also confirm that the optimal condition for preparing the CZK materials is the calcination at 700°C.

Figure 6: XRD patterns of CZK materials preheated at (a) 600, (b) 700, and (c) 850°C. +: mullite, ●: Na-P type zeolite or phillipsite, △: analcime.

Figure 7: MB equilibrium adsorption curves of CZK materials before (filled) and after (open) hydrothermal treatment. Calcination temperatures are 600 (squares), 700 (circles), and 850 (triangles)°C.
4 Conclusions

We succeeded in the preparation of the carbon/zeolite hybrid bulk materials from coal fly ash and sawdust, which are typical industrial solid wastes in Japan, by the hybrid process of calcination under N₂ atmosphere and alkali-hydrothermal treatment. Activator (Na₂CO₃ or K₂CO₃) for reagent activation during calcination was found to accelerate the activation reaction on the carbonized SD surface and increase the specific surface area originated from carbon species. Zeolite phases formed by the alkali-hydrothermal treatment changed by activator reagents for carbonaceous materials. In the case of Na₂CO₃ activator, the faujasite type zeolite with larger pore size was formed. The analcime with smaller pore size was prepared in the case of K₂CO₃ activator. We conclude that the hybrid process of calcination and hydrothermal treatment can control not only activation of the carbonized SD surface, but also zeolite phases formed.

The CZ bulk materials prepared in the present study possess hydrophobic adsorption ability due to the activated carbon and also cation exchangeable ability originated from zeolite. Therefore, such adsorbent material prepared from the industrial solid wastes would contribute to the production of low-cost material for cleaning up water and/or atmospheric air polluted by various contaminants.

References
