Purification of combustion waste gas using ecofunctional ceramics in the high temperature range

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Abstract

For the purpose of the development of new ecofunctional ceramics with removal performance for toxic substance included in combustion waste gas, hydroxyl sodalite (Na₈Al₆Si₆O₂₄(OH)₂) and hydrogrossular (Ca₃Al₂(SiO₄)₀.₈(OH)₈.₈) were investigated. It was found that these materials each had a function of chlorine fixation, copper fixation and the control of dioxin formation. Hydroxyl sodalite had micro-pore of nanometer order (β-cage) in the structure, and the chlorine ions were fixed in the pore above 400°C. The quantity of fixed chlorine with increased with increasing reaction temperature, and was largest with 7.3wt% at 800°C. The fixation of the copper progressed by the substitution with sodium ion, and the substitution quantity increased with increasing reaction temperature, the quantity was 10.5wt% of CuO at 900°C. On the other hand, hydrogrossular changed to the mayenite phase (Ca₁₂Al₁₀Si₄O₃₅) after heating above 700°C. The mayenite had the micro-pore that the chlorine ion was fixed in the structure. The drastic decrease in the dioxin concentration was confirmed by using the ecofunctional ceramics in the garbage incineration.

Keywords: hydroxyl sodalite, hydrogrossular, micro-pore, fixation of toxic material, oxygen radical.
1 Introduction

Recently, the environmental pollution by dioxins becomes serious in Japan. It is important to purify the combustion waste gas discharged by the garbage incineration, because main dioxins source originates from the garbage incineration. The much research on the removal of the toxic substance included in the combustion waste gas until now, and the research result has been used practically today. For example, it is possible to mention the removal of HCl gas using slaked lime, the adsorption removal of dioxins using active carbon, the decomposition removal of dioxins using catalyst, the elution prevention by stabilization of heavy metals adsorbed on fly ash, and the others. These purification technologies are processing technologies in low temperature of about 200°C or ordinary temperature. It seems to produce many advantages, if purification treatment of the combustion waste gas can be realized in the high temperature region. Following possibilities are considered as advantages. The efficiency improvement of heat exchange and the life-lengthen of heat exchanger and incinerator, etc. by controlling high temperature corrosion caused by acid gases, the control of dioxins formation by the removal of dioxin precursor, the pollution control of fly ash by dioxins formation control and heavy metal removal, and the others.

We investigated that HCl, copper and hydrocarbons included in the combustion waste gas were removed using ecofunctional ceramics, hydroxyl sodalite and hydrogrossular, in the high temperature range above 400°C in order to purify the combustion waste gas and control the dioxins formation.

2 Experimental

2.1 Sample preparation

Preparation of hydroxyl sodalite (Na₈Al₆Si₆O₂₄(OH)₂) was as follows. The kaolinite (Al₂(Si₂O₅)(OH)₄) was used as Al and Si source, and NaOH was used in the Na source. A mixed paste of kaolinite and NaOH was prepared in the mole ratio of 3:10. The ratio of NaOH added was in considerable excess of that theoretically required. The hydroxyl sodalite was synthesized by heat treatment (100°C, 24h) of the mixed paste in an oven. After the hydroxyl sodalite was synthesized, and further, sufficiently washed in the distilled water to remove an excess of NaOH.

Hydrogrossular (Ca₃Al₂(SiO₄)₀.₈(OH)₈.₈) was synthesized by the hydrothermal reaction of a stoichiometric mixture of alumina-sol, amorphous silica and CaO. The mixture was put in a teflon-lined stainless steel autoclave with distilled water. The water to solid ratio was 12:1 weight/weight. The autoclave was placed in the temperature-controlled oven, the temperature of which was controlled to increase from room temperature to 200°C in 2 hours. The mixture was then kept at 200°C for 15hours. The solid product was separated by filtration and dried at 110°C for 24hours.
2.2 Reaction with HCl gas at high temperature

2.2.1 A small-sized fixed bed reactor
A small-sized fixed bed reactor was used to examine the reaction between HCl gas without the moisture and hydroxyl sodalite and hydrogrossular in the temperature range from 400 to 900°C. The HCl reaction test was done as follows: A quartz glass tube packed by a sample of 0.5g was placed in the tubular electric furnace, then the sample was heated up to desired temperature in flowing dry N₂. After the sample temperature reached to desired temperature, HCl of 1000ppm was flowed for 3hours at 200ml/min flow rate.

2.2.2 A medium-sized vertical reactor
The experiment was started by heating the vertical tubular furnace at 700 or 800°C under flowing air of 45l/min. The synthetic gas, HCl:1000ppm, O₂:10vol%, CO₂:10vol%, H₂O:10vol%, N₂:balance, was introduced into the quartz glass reactor of diameter 0.1m and of length 4.5m. Hydrogrossular was introduced into the reactor at 0.4, 0.8, 1.2 and 1.6g/min. Rough drawing of the reactor and the photograph of the equipment are shown in fig.1 and photograph 1, respectively.

2.2.3 A large-sized fluidized bed combustor
Rough drawing of the combustor used is shown in fig.2. RDF made from the mixture of polyvinyl chloride, plastics waste and paper was burnt in a 1.2×1.2×9m bubbling type fluidized bed combustor. The gas flow rate was 500Nm³/h and the temperature of combustion was 750±50°C. The concentration of HCl was continuously recorded. Hydroxyl sodalite and hydrogrossular powder was introduced into the combustor at 6.2kg/h.
2.3 Reaction with CuCl\textsubscript{2} at high temperature

Two alumina boats respectively filled by 0.5g hydroxyl sodalite and 0.5g CuCl\textsubscript{2} were loaded in the tubular electric furnace, then the reaction of hydroxyl sodalite and CuCl\textsubscript{2} was carried out in the temperature range from 400 to 900\degree C in flowing the mixed gas consisted of 10vol\% O\textsubscript{2}, 10vol\% CO\textsubscript{2}, 10vol\% H\textsubscript{2}O, 1000ppm HCl and N\textsubscript{2} (balance). The flow rate of mixed gas was 500ml/min, and the reaction time was 1 hour. After the reaction was finished, the hydroxyl sodalite recovered was analyzed by XRF.

![Figure 2: Rough drawing of a large-sized fluidized bed combustor.](image)

2.4 Measurement

Thermal decomposition behavior, crystal structure and chemical composition of samples before and after reaction were examined by TG-DTA, XRD and XRF, respectively.

3 Results and discussion

3.1 Fixation performance of Cl\textsuperscript{−} ion using the small-sized fixed bed reactor

3.1.1 Hydroxyl sodalite

When hydroxyl sodalite reacts with HCl gas, OH\textsuperscript{−} ions are replaced with Cl\textsuperscript{−} ions in the β-cage of sodalite structure and it becomes sodalite (Na\textsubscript{8}Al\textsubscript{6}Si\textsubscript{6}O\textsubscript{24}Cl\textsubscript{2}) (Equation 1) [1]. The lattice constant (a\textsubscript{0}) of sodalite structure became large from 8.86 to 9.04Å according to substitution between OH\textsuperscript{−} (ionic radius: 1.32 Å) and Cl\textsuperscript{−} ion (1.81 Å).

\[
\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}(\text{OH})_2 + 2\text{HCl} \rightarrow \text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{Cl}_2 + 2\text{H}_2\text{O}
\]

(1)

The relationship between the amount of Cl\textsuperscript{−} fixed in sodalite structure and the reaction temperature is shown in fig.3. The weight ratio of Cl\textsuperscript{−} ion was measured by XRF, and the weight ratio to the sodalite (wt%) was regarded as the amount of Cl\textsuperscript{−} fixed. The amount of Cl\textsuperscript{−} fixed increased with increasing the reaction temperature, however it was drastically decreased after the highest value was
shown at 800°C. The amount of Cl\textsuperscript{−} fixed at 900°C was zero. The amount of Cl\textsuperscript{−} fixed at 800°C was 7.3wt%, this value was correspondent to the Cl\textsuperscript{−} weight ratio in sodalite.

![Figure 3: The relationship between the amount of Cl\textsuperscript{−} fixed in sodalite structure and the reaction temperature.]

According to the measurement result of TG-DTA of hydroxyl sodalite, the dehydration reaction which originated for OH\textsuperscript{−} occurred at 260°C, and hydroxyl sodalite made phase change in carnegieite (NaAlSiO\textsubscript{4}) at 877°C. As a result of examining the reaction of carnegieite and HCl, the carnegieite already did not react with HCl in the temperature range from 400 to 900°C.

### 3.1.2 Hydrogrossular

From the TG-DTA measurement of hydrogrossular, following fact became clear. The endothermic peaks at 320 and 680°C recorded in DTA were able to be attributed to the release of OH radical. Hydrogrossular was transformed into anhydrous mayenite (Ca\textsubscript{12}Al\textsubscript{10}Si\textsubscript{4}O\textsubscript{35}) through hydrous mayenite (Ca\textsubscript{12}Al\textsubscript{10}Si\textsubscript{4}O\textsubscript{32}(OH)\textsubscript{6}) phase. The ideal phase transition of hydrogrossular with increasing temperature can be given by equation 2 and 3, respectively [2,3].

\[
5\text{Ca}_3\text{Al}_2(\text{SiO}_4)_{0.8}(\text{OH})_{8.8} \rightarrow \text{Ca}_{12}\text{Al}_{10}\text{Si}_4\text{O}_{32}(\text{OH})_6 + 3\text{CaO} + 19\text{H}_2\text{O} \text{ at 320°C (2)}
\]

\[
\text{Ca}_{12}\text{Al}_{10}\text{Si}_4\text{O}_{32}(\text{OH})_6 \rightarrow \text{Ca}_{12}\text{Al}_{10}\text{Si}_4\text{O}_{35} + 3\text{H}_2\text{O} \text{ at 680°C (3)}
\]

The XRD patterns of hydrogrossular reacting with HCl were measured at the ambient conditions after cooling from each reaction temperature to room temperature. At the reaction temperature above 400°C, the main phase was wadalite (Ca\textsubscript{12}Al\textsubscript{10}Si\textsubscript{4}O\textsubscript{32}Cl\textsubscript{6}), and the second phase corresponding to CaCl\textsubscript{2} \cdot 2H\text{O} was observed. Since CaCl\textsubscript{2} is highly hygroscopic, it may take up moisture and form CaCl\textsubscript{2} \cdot 2H\text{O}. The chemical composition of the sample, after removing the second phase (CaCl\textsubscript{2} \cdot 2H\text{O}) by washing in distilled water, was Ca\textsubscript{12}Al\textsubscript{9.9}Si\textsubscript{4.05}O\textsubscript{32}Cl\textsubscript{5.9} (Wadalite), which has chlorine content of 13.2wt%. The HCl gas is efficiently remove from the inlet gas as Ca\textsubscript{12}Al\textsubscript{9.9}Si\textsubscript{4.05}O\textsubscript{32}Cl\textsubscript{5.9} and CaCl\textsubscript{2} above 400°C.
On the basis of the results obtained, the reaction formula of hydrogrossular and HCl is shown in equation 4 and 5 [2,3].

\[
\begin{align*}
\text{Ca}_{12}\text{Al}_{10}\text{Si}_{4}\text{O}_{32}(\text{OH})_6+3\text{CaO}+12\text{HCl} & \rightarrow \text{Ca}_{12}\text{Al}_{10}\text{Si}_{4}\text{O}_{32}\text{Cl}_6+3\text{CaCl}_2+9\text{H}_2\text{O} \\
400\text{~}650^\circ\text{C} & \quad (4) \\
\text{Ca}_{12}\text{Al}_{10}\text{Si}_{4}\text{O}_{35}+3\text{CaO}+12\text{HCl} & \rightarrow \text{Ca}_{12}\text{Al}_{10}\text{Si}_{4}\text{O}_{32}\text{Cl}_6+3\text{CaCl}_2+3\text{H}_2\text{O} \\
\text{above } 700^\circ\text{C} & \quad (5)
\end{align*}
\]

3.2 HCl removal performance using the medium-sized vertical reactor

In the medium-sized vertical reactor with flowing synthetic gases, the concentration of HCl at 700 and 800°C with introducing hydrogrossular of 0.4~1.6g/min was measured. The HCl was efficiently removed from the inlet gas, and the HCl concentration decreased with increasing the amount of introducing. In fig.4, the result of introducing hydrogrossular of 0.4 (a) and 1.6g/min (b) is shown. The HCl concentration at 800°C was only decreased at a half quantity in comparison with the concentration at 700°C. This result is understood in terms of the fact that at 800°C, H$_2$O only suppresses CaCl$_2$ formation but not wadalite formation [4,5,6].

![Figure 4: The effect of hydrogrossular introducing for the HCl concentration reduction.](image)

3.3 Reaction of hydroxyl sodalite and CuCl$_2$

After the reaction of hydroxyl sodalite and CuCl$_2$ in the temperature range from 400 to 900°C was finished, the hydroxyl sodalite recovered was analyzed by XRF. The result of analysis is shown in table 1 and fig.5. The content of Al$_2$O$_3$ and SiO$_2$ after the reaction was almost same, and however, the content of Na$_2$O decreased with rising the reaction temperature. There was the increase of CuO content with the decrease of Na$_2$O. The relation between CuO content and Na$_2$O content showed the reverse correlation, as it was clear in fig.5. As a result of the similar experiment using sodalite (Na$_8$Al$_6$Si$_6$O$_24$Cl$_2$), the CuO content at 700°C
was 5.0wt%. This value was almost equal to it of hydroxyl sodalite (5.3wt%). From these results, it was concluded that hydroxyl sodalite and sodalite could react with CuCl₂ at high temperatures over 400°C, and Na cations in hydroxyl sodalite and sodalite were substituted by Cu cations.

Table 1: Analysis result of hydroxyl sodalite after reaction with CuCl₂.

<table>
<thead>
<tr>
<th>Reaction temperature/˚C</th>
<th>Reaction time/Hour</th>
<th>Analysis value / wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CuO</td>
</tr>
<tr>
<td>400</td>
<td>1</td>
<td>0.2</td>
</tr>
<tr>
<td>500</td>
<td>1</td>
<td>2.4</td>
</tr>
<tr>
<td>700</td>
<td>1</td>
<td>5.3</td>
</tr>
<tr>
<td>800</td>
<td>1</td>
<td>6.7</td>
</tr>
<tr>
<td>900</td>
<td>1</td>
<td>10.5</td>
</tr>
</tbody>
</table>

Though in the analysis result, there is the existence of Cl in hydroxyl sodalite, Cl⁻ ions from CuCl₂ and /or HCl seemed to react.

Figure 5: The relationship between Na₂O, CuO content in hydroxyl sodalite and reaction temperature.

3.4 The combustion waste gas purification performance using the large-sized fluidized bed combustor

In the large-sized fluidized bed combustor, table 2 summarizes the composition of the combustion waste gas from RDF in the combustor. After introducing hydroxyl sodalite or hydrogrossular, the HCl concentration decreased from 151ppm to 13ppm for the former and from 174ppm to 35ppm for the latter. The dioxin concentration (0.21ng-TEQ/Nm³) without the introduction of hydrogrossular were (sampling point (a) in Table 2) was lower than that with hydrogrossular. A more oxidizing condition for combustion, as a lower CO concentration (687ppm versus 1010ppm) suggested, was a possible cause for the reduction of dioxin formation. It was noted that the formation of dioxin at the
inlet of the gas cooler was more pronouncedly suppressed with the use of hydrogrossular than without it, although the combustion conditions were different from each other. This suppression should result from capturing Cl$^-$ with hydrogrossular at high temperatures, by which the formation of dioxin was avoided. It is also probable that the oxidative decomposition of dioxin occurs, even if it is formed during the combustion of RDF. This is because mayenite (Ca$_{12}$Al$_{10}$Si$_4$O$_{35}$), which is formed by the thermal decomposition of hydrogrossular, has the ability for the oxidative decomposition of chlorinated compounds to CO$_2$ and H$_2$O probably due the superoxide anion (O$_2^-$) and peroxide anion (O$_2^{2-}$) present in it [7,8]. On the other hand, since hydroxyl sodalite also has the possibility of occluding the oxygen radicals, it is considered that the similar phenomenon occurs even in hydroxyl sodalite. On this point, the research has been continued today. Anyway, it was confirmed that the amount of dioxin could be decreased by simply introducing hydrogrossular or hydroxyl sodalite into a conventional combustor with no modification.

Table 2: Composition of the combustion waste gas.

<table>
<thead>
<tr>
<th>Sampling point (a)</th>
<th>Blank</th>
<th>Hydroxyl sodalite</th>
<th>Hydrogrossular</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dioxin (ng-TEQ/Nm$^3$)</td>
<td>0.21</td>
<td>0.06</td>
<td>1.2</td>
</tr>
<tr>
<td>HCl (ppm)</td>
<td>174</td>
<td>151</td>
<td>114</td>
</tr>
<tr>
<td>O$_2$ (%)</td>
<td>2.4</td>
<td>3.7</td>
<td>2.3</td>
</tr>
<tr>
<td>CO (ppm)</td>
<td>687</td>
<td>999</td>
<td>1010</td>
</tr>
<tr>
<td>Sampling point (b)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dioxin (ng-TEQ/Nm$^3$)</td>
<td>12</td>
<td>4.2</td>
<td>4.6</td>
</tr>
<tr>
<td>HCl (ppm)</td>
<td>174</td>
<td>13</td>
<td>35</td>
</tr>
<tr>
<td>O$_2$ (%)</td>
<td>3.2</td>
<td>3.7</td>
<td>2.3</td>
</tr>
<tr>
<td>CO (ppm)</td>
<td>741</td>
<td>1020</td>
<td>&gt;1100</td>
</tr>
<tr>
<td>SO$_2$ (ppm)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>NO$_2$ (ppm)</td>
<td>18</td>
<td>11</td>
<td>21</td>
</tr>
</tbody>
</table>

4 Conclusions

New ecofunctional ceramics, hydroxyl sodalite and hydrogrossular were developed. As a result of the test in the incinerator with plant scale, it was proved that new ecofunctional ceramics could decrease each concentration of HCl and dioxin contained in the combustion waste gas at high temperature. In addition, it was found that hydroxyl sodalite fixed the copper in vapor phase at high temperatures.
References


