Study on Gas Adsorptive Property of Cupola Dust

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Gas adsorptive properties of dust, which is exhausted from cupula, have been investigated at room temperature. The cupula dust adsorbed some gases, and in particular hydrogen sulfide (H₂S). The adsorptive mechanism for H₂S has been examined through the characterization of the dust by X-ray fluorescence analysis, X-ray diffraction, transmission electron microscopy, measurement of adsorptive capacity, etc. Consequently, it was found that the property was induced by the spinel nanocrystals with 10-50 nm in dimension such as (Mn,Fe₁₋ₓ)₂O₃ solid solutions in the dust. Furthermore, the characterization revealed that the adsorptive capacity of the dust for H₂S was promoted by the NaOH treatment. In addition, it was found that the Mn content of the dust correlates with the adsorptive capacity for H₂S. [Received July 29, 2003; Accepted January 5, 2004]

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1. Introduction

Treatment of waste is one of the important subjects for ensuring a sustainable environment. Lots of research is going on in the area of recovering general and industrial wastes as resource. For example, wastes containing Si and Al such as waste incineration fly ash, coal fly ash, etc. are proposed to be converted into zeolitic compounds¹⁻⁶ and used as raw materials for cement.⁷

Slag exhausted from steel industries and foundries is also utilized in a similar way. However blast furnace and cupola dusts, which are formed by the solidification of gas exhausted from blast furnace and cupola, respectively, have fallen behind in resource recovery, in spite of containing useful elements. There are few reports describing available recycling process of the dusts, especially cupola dust, because Zn in the cupula dust restricts reuse as follows. When the dust was used as a raw material for cement, Zn has a harmful influence on cement quality, and Zn content is, moreover, too low to smelt zinc from the dust. Thus, as over hundreds of thousands of tons of the cupula dust per year is landfill in Japan, and the space available for landfill disposal is restricted, immediate countermeasures are urgent for the preservation of the environment.

Cupula dust was investigated from different angles so as to find its most efficient use. Consequently, the cupula dust was discovered to have gas adsorptive ability. In this paper, we describe the adsorptive properties of the cupula dust for poisonous gases, especially hydrogen sulfide, from the standpoint of structure and composition of the dust.

2. Experimental

2.1 Materials

Cupula dust used here was collected from the bag filter, which is located at the end of the cooling system which is interconnected to the top of the cupula in Aisin Takaoka Co. Ltd., (Toyota, Japan). Metal vapor exhausted from the cupula is solidified through the cooling system, and the solidified particles, which we call cupula dust, are trapped by the bag filter.

2.2 Analysis

Chemical compositions of the dust were analyzed by an X-ray fluorescence technique on a Rigaku RIX3000 spectrometer. Crystalline phases in the dust were identified by powder X-ray diffraction (XRD), using a Rigaku RINT2100/PC diffractometer with monochromated CuKα radiation.

Microstructures of the dust were examined by transmission electron microscopy (TEM), using a Hitachi HF-2000 transmission electron microscope equipped with a field emission type electron gun operated at 200 kV. The dust specimen for the observation was prepared by ion-milling method. Chemical components of the microstructure were analyzed by energy dispersive X-ray fluorescence technique (EDX), using a Xevis Sigma analyzer. K-factor correction for O atom was made in the EDX analyses, because the quantitative accuracy of EDX is low for light elements. Namely, the visual field, where Si and O atoms were only detected, was regarded as SiO₂. And, the data obtained from the field consisting of Si and O atoms were used as references for correcting the k-factor for other O atom in crystalline fields.

Specific surface area of the dust was measured by nitrogen adsorption isotherm measurement with the BET method, using a BEL-Japan BELSORP18PLUS.

2.3 Gas adsorption

Gas adsorptive properties of the dust were examined in two ways. In the first way, poisonous gases balanced with nitrogen (N₂) gas were used such as 500 ppm hydrogen sulfide (H₂S), 500 ppm ammonia (NH₃), 500 ppm sulfur dioxide (SO₂), 475 ppm nitrogen dioxide (NO₂), 60 ppm trimethylamine ((CH₃)₂N), and 8.5 ppm dimethyl disulfide (C₂H₅S₂). 3 L of each poisonous gas and 0.5 g of each dust were fed into a gas gathering bag made of PET, and the concentration of the residual gas in the bag was measured by a gas detectable tube after 2 h. The adsorptive properties of the dust against the poisonous gases were evaluated by the removal ratios.

In the second way, the removal amounts of the dust for H₂S gas were examined at room temperature by the following gravimetric method. 0.1 g of the dust was dried at 303 K under vacuum lower than 5 Pa in a glass tube, and then water vapor was fed into the glass tube, because the adsorption doesn’t occur in dry circumstances. The relative pressure (P/P₀) was controlled at about 0.6, referring to the mean humidity in the air. The weights of dry dust under vacuum and wet dust after reaching equilibrium were measured. After the measurements, 20 kPa of pure H₂S gas was fed into a glass tube. The weight of H₂S adsorbed on the wet dust was measured after 24 h, and the weight ratio of net adsorbed H₂S to the dry dust was regarded as H₂S adsorptive capacity.
2.4 Hydrothermal treatment
The dust was hydrothermally treated in the presence of 0.5–5 M (mol·dm⁻³) NaOH (Kanto Kagaku) aqueous solution. The solid/liquid ratio was set at 1/30–1/4. The treatment was performed at 353–398 K for 4.5–41 h in a Teflon-lined autoclave under an autogeneous pressure with continuous stirring. The products after the treatment were filtered and repeatedly washed with deionized water. The resulting materials were dried at 333 K for 24 h and ground for further analyses, i.e. XRD, TEM-EDX and measurement of adsorptive capacity for H₂S gas.

3. Results and discussion
3.1 Adsorptive property
The gas adsorptive property of the dust is shown in Fig. 1. The dust completely adsorbed H₂S in the gas gathering bag within 2 h. Although it also behaved as a good adsorbent for NH₃, SO₂ and NO₂, it showed low removal effectiveness for (CH₃)₂N and C₂H₂S₂.
As the dust adsorbed H₂S most of all, compared with other gases examined here, the adsorptive capacity of the dust for H₂S were evaluated by gravimetric method. About 0.08 g of H₂S was estimated to be adsorbed on 1 g of the dry dust from the measured results.

3.2 Structure and composition
Representative chemical components of the dust are listed in Table 1, and XRD patterns of the dust before and after adsorbing H₂S are illustrated in Fig. 2. The main crystalline phase in the dust was identified as a spinel, accompanied by small amounts of SiO₂ and Zn₂SiO₄, corresponding to the analytical results that the dust includes Si, Fe and Zn as main elements, and much Mn next to them. The spinel was supposed to be composed of Fe₂Zn₃O₄. Small broad peaks were observed at around 2θ = 28° on the XRD pattern of the dust after adsorbing H₂S. This suggests that some compounds in the dust react with H₂S.

As the chemical composition of waste is an important factor in the development of a resource recovery process, the change in the chemical compositions of the dust had been checked for 6 months. From the results, no distinct change was detected.

Figure 3 illustrates TEM image of the dust. The TEM revealed that the dust consisted of spherical particles with 50–300 nm in diameter, where many nanocrystals with 10–50 nm in dimension were wrapped in a shell, which was revealed as an amorphous phase by electron diffraction. The non-crystalline shell of spherical particle was analyzed to be composed of Si and O with the Si/O ratio of 1/2, i.e. SiO₂, by the EDX. The nanocrystals in the spherical particles were evaluated by electron diffraction, referring to XRD patterns. Consequently, most of them were identified as spinel, and some of them were identified as Zn₂SiO₄.

The spinel nanocrystals marked in Fig. 3(A–C) were assayed by the EDX. The EDX revealed that O and total metal contents were about 60 and 40 atom%, respectively, which are close to those in the ideal spinel compound (Mn-MnO₄). Thus, the fractions of Mn, Fe and Zn in the metallic constituent were estimated, assuming that the spinel nanocrystals were stoichiometric compounds, though there remains possibility of non-stoichiometric compounds. Table 2 lists the resulting fractions amounted to 100 atom% in the spinel nanocrystals represented by A, B, C, C₁ and C₂ for the dust, suggesting that main element is Fe. If Fe occupies the M¹ site in the spinel structure, the fraction of Fe becomes 66.7 atom%.

On the other hand, as it is known that Zn preferentially occupies the M³ site in the spinels such as ZnMn₂O₄ and ZnFe₂O₄,⁴ the fractions of Zn is 33.3 atom%. The estimated fractions of Fe and Zn in those nanocrystals were, however, rather lower. These spinel nanocrystals were, therefore, identified as mainly substitutional solid solution of Zn₉Fe₉O₁₄, where the M¹ and M³ sites are partly occupied by Mn, namely (Mn, Zn)₉₋ₓ (Mn, Fe)ₓ O₁₄ solid solutions.

The spinel nanocrystals in the dust were considered to play an important role in adsorbing H₂S, referring to the studies on H₂S adsorptions of ZnFe₂O₄ and CuMn₂O₄ under high temperature conditions.⁵–¹² It is, therefore, of interest.

![Fig. 1. Removal ratio of cupula dust for poisonous gases.](image)

![Fig. 2. XRD patterns of cupula dust before and after adsorbing H₂S. (a) Before adsorbing H₂S, (b) after adsorbing H₂S.](image)

**Table 1. Chemical Components of Cupula Dust**

<table>
<thead>
<tr>
<th>Component</th>
<th>Content / mass%</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>39.5</td>
</tr>
<tr>
<td>Mg</td>
<td>0.6</td>
</tr>
<tr>
<td>Al</td>
<td>2.2</td>
</tr>
<tr>
<td>Si</td>
<td>15.5</td>
</tr>
<tr>
<td>P</td>
<td>0.1</td>
</tr>
<tr>
<td>S</td>
<td>0.3</td>
</tr>
<tr>
<td>Cl</td>
<td>0.9</td>
</tr>
<tr>
<td>K</td>
<td>1.3</td>
</tr>
<tr>
<td>Ca</td>
<td>4.1</td>
</tr>
<tr>
<td>Mn</td>
<td>7.8</td>
</tr>
<tr>
<td>Fe</td>
<td>11.8</td>
</tr>
<tr>
<td>Cu</td>
<td>0.1</td>
</tr>
<tr>
<td>Zn</td>
<td>15.3</td>
</tr>
<tr>
<td>Sn</td>
<td>0.1</td>
</tr>
<tr>
<td>Pb</td>
<td>0.4</td>
</tr>
</tbody>
</table>
to further examine $\text{H}_2\text{S}$ adsorptions of the spinel nanocrystals.

3.3 Extraction of spinel nanocrystals

The dust was hydrothermally treated in the presence of NaOH solution to extract the spinel nanocrystals. Figure 4 illustrates the fractions of Si, Mn, Fe, and Zn in the NaOH-treated dust analyzed by an X-ray fluorescence technique. The higher the concentration of NaOH solution is, the lower the fractions of Si and Zn in the dust are. After 5 M NaOH treatment, the fractions of Mn, Fe and Zn became about 28, 31 and 19 atom%, respectively. The XRD patterns described in Fig. 5 exhibited that crystalline $\text{SiO}_2$ and $\text{Zn}_2\text{SiO}_4$ phases decreased with increasing NaOH concentration, and the crystalline spinel phase only remained after 5 M NaOH treatment. The fractions of Mn, Fe and Zn were, therefore, converted to about 36, 40 and 24 atom%, respectively, provided that they were components of the spinel. The fractions converted are in close agreement with those listed in Table 2. Specific surface areas of the dusts with 5 M NaOH treatment and without were measured. The former was 38.0 $\text{m}^2/\text{g}$ and the latter was 6.5 $\text{m}^2/\text{g}$. These results suggest that the spinel nanocrystals are successfully extracted by the NaOH treatment. Figure 6 shows

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**Table 2. Metal Component Fractions in Nanocrystals up to 100 atom%**

<table>
<thead>
<tr>
<th>Content / atom%</th>
<th>A</th>
<th>B</th>
<th>C1</th>
<th>C2</th>
<th>C3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>25</td>
<td>21</td>
<td>36</td>
<td>35</td>
<td>33</td>
</tr>
<tr>
<td>Fe</td>
<td>45</td>
<td>48</td>
<td>40</td>
<td>43</td>
<td>43</td>
</tr>
<tr>
<td>Zn</td>
<td>30</td>
<td>31</td>
<td>24</td>
<td>22</td>
<td>24</td>
</tr>
</tbody>
</table>

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![Fig. 4](image4.png) Fig. 4. Fraction of Si, Mn, Fe and Zn in NaOH-treated cupola dust up to 100 atom%.

![Fig. 5](image5.png) Fig. 5. XRD patterns of cupola dust before and after NaOH-treatments. (a) Before treatment, (b) after 1 M treatment and (c) after 5 M treatment.

![Fig. 6](image6.png) Fig. 6. TEM image of cupola dust after 5 M NaOH-treatment. A is a separated nanocrystal and B is a non-crystalline $\text{SiO}_2$. 

TEM image of the 5 M NaOH-treated dust. The TEM revealed that most of the spinel nanocrystals were separated from non-crystalline SiO2 shells, and small amounts of non-crystalline SiO2, which corresponded to Si detected by an X-ray fluorescence technique, still stay as binders among the spinel nanocrystals. When the dust was treated by 0.5 M NaOH, it was found that any spinel nanocrystals were hardly separated, although the surface of the spherical particles turned rough, and their shapes were deformed.

The effect of NaOH treatments on the adsorptive capacity for H2S was examined. Figure 7 presents the adsorptive capacities of the dust for H2S before and after NaOH treatments. Although the adsorptive capacity of the 0.5 M NaOH-treated dust was similar to that of the untreated, those of the dust treated with 1 M NaOH or above drastically increased. The main factor inducing the adsorptive function for H2S was proved to be the spinel nanocrystals such as (Mn-Zn1−x) (Mn, Fe1−y)3O4 solid solutions in the dust.

Furthermore, the dusts were treated with 5 M NaOH in various reaction conditions, such as changing dust lots, solid/liquid ratios, reaction temperatures and reaction times. The adsorptive capacity of each dust for H2S was measured, and Fig. 8 shows the relations between the contents of Si, Fe, Zn and Mn in each dust and the adsorbed H2S weight ratio. Fig. 8 represents a high correlation between Mn content and the adsorbed H2S weight ratio, but the other components have no correlation with the adsorbed H2S weight ratio.

Figure 9 illustrates XRD patterns of the NaOH-treated and untreated dusts after contacting with H2S. New broad peaks at around 2θ = 28°, 47° and 55° assigned to MS (M = Mn, Fe and Zn) appeared, and the spinel decreased with increasing concentration of NaOH used in the treatments. From the result, H2S was found to be eliminated by the chemical reaction with the spinel nanocrystals in the dusts.

On the other hand, the adsorptive capacities of ZnFe2O4 (Johnson Matthey) and Fe-based adsorbent (Nissan Girdner Catalyst) on the market for H2S were measured to be about 0.29 and 0.27 g per 1 g, respectively. By controlling the hydrothermal condition, the adsorptive capacity of the NaOH treated dust was concluded to be comparable to those of the products now on the market in spite of including non-crystalline SiO2.

4. Conclusions
The adsorptive properties of the dust exhausted from cupola have been examined for poisonous gases at room temperature, aiming at resource recovery. As a result, it was found that this dust had excellent removal ability for H2S. Then the investigation on adsorptive mechanism from the standpoints of the composition and structure of the dust made the followings clear. The dust mainly consists of fine spherical particles including the spinel nanocrystals such as (Mn-Zn1−x) (Mn, Fe1−y)3O4 solid solutions. The spinel nanocrystals act as a main factor of eliminating H2S through the chemical reaction, and Mn content of the nanocrystal is found to correlate with the adsorptive capacity for H2S. A comparison was made of the removal ability of dust and other H2S adsorbents currently on the market. The results showed that the NaOH treated dust compared favorably with other H2S adsorbents and could be practically utilized as an H2S adsorbent at room temperature.
References


Fig. 9. XRD patterns of NaOH-treated and untreated cupola dust after contacting with H₂S. (a) Untreated, (b) 1 M NaOH treatment and (c) 5 M NaOH treatment. MS denotes FeS, MnS and ZnS.