PREPARATION OF ZINC FERRITE IN THE PRESENCE OF CARBON MATERIAL AND ITS APPLICATION TO HOT-GAS CLEANING

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Introduction
Increasing attention is being paid to integrated gasification combined cycle (IGCC) process and gasification-molten carbonate fuel cell (MCFC) technology as one of the most promising technologies to reduce CO₂ emission. For these technologies, several thousands ppm of hydrogen sulfide containing in an effluent gas from gasifier must be efficiently removed to several ppm for IGCC and <1 ppm for MCFC at a high temperature. Zinc ferrite (ZnFe₂O₄) is known to be one of the candidates for hydrogen sulfide removal. In addition to zinc ferrite, various sorbents, such as manganese oxides and zinc titanate, have been investigated. We have recently found that activated carbon-supported ZnFe₂O₄ could be prepared at much lower calcination temperature required for dry process ferrite synthesis and that its absorption capacity was much higher than that of dry process ferrite.

In the present work, activated carbon-, activated carbon fiber-, and coal-supported zinc ferrite were prepared at a low temperature in order to obtain an effective absorbent for H₂S. In addition to zinc ferrite, activated carbon and Yallourn coal char prepared by various methods. In the cases of ferrites loaded on organic support, oxide content in the total absorbent was evaluated based on the weight decreases of the samples, by burning the organic part by using a thermogravimetric balance in a flowing air. The surface areas of zinc ferrites prepared by the presence of ACF and AC (Samples D, F, and G) were higher than those zinc ferrites (Samples A, B, and C), which were prepared without carbon materials. The surface area of ZnFe₂O₄/ACF reached 1190 m²/g due to a large amount of remained high surface area ACF. Surface areas decreased to 50 m²/g with a decrease in the amount of carbon remaining (1-14 %). XRD analyses exhibited only diffraction peaks ascribed to ferrite phase after the calcinations in air at above 500 °C, with the exception of some cases. Samples E, F, and H showed very weak diffraction peaks ascribed to ZnO and Fe₂O₃, in addition to those of zinc ferrite.

Experimental
Preparation of sorbent.

Homogeneous precipitation method. Into a mixed solution of Fe(NO₃)₃ and Zn(NO₃)₂ (150 mmol/L, 80 mL), 0.04 mmol of urea and 0.3 g of activated carbon (AC, Wako Pure Chemical Industries, Ltd., 100-mesh pass, 993 m²/g), or Yallourn coal (YL, C 66.3; H 4.70; N 0.48; S 0.26 daf%; Ash 2.0 daf%, 100-mesh pass) was added. The mixture was heated at 80 °C for 2h. During this stage, Zn(OH)₂ and Fe(OH)₃ were precipitated on AC, ACF, or YL coal. The mixture was washed at 70 °C in vacuo, and then it was calcined at 400 or 500 °C in air for 2h.

Coprecipitation method. A 0.3 g of AC or YL coal was added into a mixed solution of Fe(NO₃)₃ (20 mmol/L, 100 mL) and Zn(NO₃)₂ (10 mmol/L, 100 mL), and then into this suspension aqueous ammonia was added until pH of the suspensate solution reaches 10. The combined precipitates were separated and dried in vacuo. The mixture was calcined at 300 or 500 °C in air for 2h.

Impregnation method. Zinc ferrite was prepared on AC or YL by the impregnation method described in the previous literature.

Characterization of sorbents. The ferrite prepared here and the metal species obtained after the absorption of hydrogen sulfide were analyzed by powder X-ray diffraction using an X-ray diffractometer (Shimadzu XRD-6000) with monochromated CuKα radiation. The surface areas of activated carbon-loaded and unloaded ferrite were measured using a Micromeritics Gemini 2375, applying adsorption isotherms of nitrogen at -196 °C to the BET equation.

Breakthrough behavior of sorbents measured by a fixed-bed reactor. The breakthrough curves were obtained by using a fixed-bed flow type reactor according to the procedure that was described in the previous paper.

Results and Discussion
Preparation and characterization of sorbents. Table 1 summarizes results of surface area and the content of oxides of various absorbents loaded on activated carbon, activated carbon fiber, and Yallourn coal char prepared by various methods. In the cases of ferrites loaded on organic support, oxide content in the total absorbent was evaluated based on the weight decreases of the samples, by burning the organic part by using a thermogravimetric balance in a flowing air. The surface areas of zinc ferrites prepared in the presence of ACF and AC (Samples D, F, and G) were higher than those zinc ferrites (Samples A, B, and C), which were prepared without carbon materials. The surface area of ZnFe₂O₄/ACF reached 1190 m²/g due to a large amount of remained high surface area ACF. Surface areas decreased to 50 m²/g with a decrease in the amount of carbon remaining (1-14 %). XRD analyses exhibited only diffraction peaks ascribed to ferrite phase after the calcinations in air at above 500 °C, with the exception of some cases. Samples E, F, and H showed very weak diffraction peaks ascribed to ZnO and Fe₂O₃, in addition to those of zinc ferrite.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sorbent</th>
<th>Method</th>
<th>Calcination temp. °C</th>
<th>Phase determined by XRD</th>
<th>S.A. m²/g</th>
<th>Oxide content wt%</th>
<th>Absorption capacity %</th>
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<tr>
<td>A</td>
<td>ZnFe₂O₄</td>
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<td>1000</td>
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<td>CoPPT</td>
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<td>Amorphous</td>
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<td>HomoPPT</td>
<td>400</td>
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a) Carried out using a fixed-bed reactor (N₂, H₂S(0.96 vol%) 5 mL/min, H₂ 2mL/min, Absorption temperature 500 °C)
PPT: Precipitation method, CoPPT: Coprecipitation method, HomoPPT: Homogeneous precipitation method, IMP: Impregnation method
Absorption behavior of hydrogen sulfide. Figure 1 shows examples of breakthrough behavior of H$_2$S using various sorbents measured at 500 °C. The horizontal axis of Figure 1 designates the absorption capacity, which was calculated assuming that all zinc and iron in the ferrite would be transformed into ZnS and FeS. The absorption capacity exceeded 100% because a part of the iron was transformed into FeS$_2$. The absorption capacity of each sorbent is shown in the last column of Table 1. The absorption capacities of hydrogen sulfide (48-49%) with unloaded zinc ferrite (Samples A and C) were lower than those (>85%) of loaded zinc ferrites. When Fe$_3$O$_4$ (Samples B and I) and ZnFe$_2$O$_4$ prepared by dry method (Sample A) were used for H$_2$S absorption, high concentrations of H$_2$S (<20 ppm) were observed until the breakthrough point. On the other hand, the absorption capacities of H$_2$S increased to nearly 100% or more with ZnFe$_2$O$_4$ prepared on AC, ACF, and YL coal (Samples E-L). These absorbents showed no H$_2$S leakage in the effluent gas (less than 1 ppm). Although the surface areas of Samples F and G were higher than those of Samples E and H-L, the absorption capacities did not change. This fact indicates that the surface area seems not to be an important factor for the high absorption capacity of H$_2$S.

To examine the effect of the absorption temperature on the absorption capacity of the sorbent, the absorption of H$_2$S was carried out with ZnFe$_2$O$_4$/YL at 400-700 °C. When hydrogen sulfide was absorbed at 400 °C and 450 °C, the absorption capacities were 116% and 120%, respectively, and then that slightly decreased to 103% with increasing the absorption temperature to 500 °C and 600 °C. An elevated absorption temperature (700 °C) decreased the absorption capacity to 63%, indicating that optimal temperature of H$_2$S removal with ZnFe$_2$O$_4$/YL is 400-600 °C.

In order to elucidate the effect of the calcination temperature of the sorbent on the absorption behavior of H$_2$S, the breakthrough curves of the YL coal-supported zinc ferrites were calcined at 500-800 °C and measured at absorption temperature of 500 °C. The absorption capacity of ZnFe$_2$O$_4$/YL gradually decreased with increasing the calcination temperature to 800 °C, indicating that crystallite size of ZnFe$_2$O$_4$ determined by XRD analyses increased. This result clearly indicates that a crystallite size of ZnFe$_2$O$_4$ seems to be important for the high absorption capacity of H$_2$S.

Regeneration and repeated use of sorbent. Regeneration and repeated use of sorbent for H$_2$S removal is crucial to practical use. In order to ascertain the possibility of regeneration of sorbent after the absorption reaction of H$_2$S, the temperature programmed oxidation of the H$_2$S absorbed ZnFe$_2$O$_4$/YL (ZnS, FeS$_2$, Fe$_2$S) was carried out using a mixed gas of Ar and O$_2$ (50 vol%). The releases of SO$_2$ and SO$_3$ were confirmed with a mass spectroscopy from 350 to 530 °C. Regeneration of H$_2$S absorbed ZnFe$_2$O$_4$/YL was carried out at 450 °C for 30 min using the fixed-bed reactor in oxygen-argon gases (O$_2$: 50 vol%, Ar: 50 vol%). According to the XRD analyses of ZnFe$_2$O$_4$/YL before the H$_2$S absorption and after four sulfurization-regeneration cycles, ZnFe$_2$O$_4$/YL exhibited diffraction peaks ascribed to ZnS and very weak diffraction peaks of ZnO and Fe$_2$O$_3$. YL coal or AC loaded ferrites could successfully be regenerated at 450 °C. YL coal was burned out during the regeneration at 450 °C in a flowing air and the amount of carbon material decreased to nearly nil. Figure 2 illustrates the breakthrough curves that were measured at 500 °C using regenerated zinc ferrite, after second (R-2), third (R-3), and fourth (R-4) regeneration cycles. The absorption capacity of hydrogen sulfide with the fresh sorbent was 90%, and repeated use of the sorbent slightly decreased the absorption capacity to 75%. However, H$_2$S concentration in the tail gas was kept very low values.

Conclusion
Zinc ferrites could be prepared on activated carbon, activated carbon fiber, and Yallourn coal. Performance of the zinc ferrite for H$_2$S absorption was evaluated using a fixed-bed flow type reactor. These absorbents efficiently remove H$_2$S at an absorption temperature of 500 °C. Coal-loaded zinc ferrite could be regenerated by air oxidation at 450 °C. The regenerated zinc ferrite can be used for repeated absorption of H$_2$S with a slight decrease in the absorption capacity.

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References

Figure 1 Breakthrough curves of H$_2$S absorption using various sorbents obtained at 500 °C. (Conditions: Ar 5 mL/min, N$_2$+H$_2$S 5 mL/min, H$_2$ 2 mL/min)

Figure 2 Breakthrough curves of H$_2$S absorption using ZnFe$_2$O$_4$/YL and regenerated