

Advanced Gas Cleaning Technology

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DRY GAS CLEANING IN COAL GASIFICATION SYSTEM FOR FUEL CELLS

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ABSTRACT

Composite sorbents, for simultaneous removal of sulfur compounds, and alkali and heavy metals from gasifier products in an integrated gasification fuel cell (IGFC) system were prepared. For desulfurization sorbents iron oxide and zinc ferrite were chosen and they are synthesized by precipitation from either ferric chloride or nitride, or ferric and zinc nitrides solution. In these solutions fine oxide particles, such as kaolinite, sepiolite, and activated clay, having the capability of alkali and heavy metal absorption were suspended. Oxide particles effectively increased the surface area of synthesized iron oxide and zinc ferrite, and increased the desulfurization capacity, as well as metal absorption ability which will be reported in our separated paper. Desulfurization capacity and crystalline phases before and after desulfurization depended on what kinds of oxide particles were suspended. Desulfurization capacity was characterized well with the specific surface area of composite sorbent.

INTRODUCTION

Hot gas cleanup is a key technology in an integrated gasification fuel cell (IGFC) system. Fuel gas products from a gasifier contains a lot of contaminants, i.e., sulfur compounds (H_2S and COS), and alkali and heavy metal compounds, which must be removed to prevent the corrosion of fuel cell electrodes. In IGFC systems wet gas purification process has been applied so far and pilot testing such as 150 t/d EAGLE Plant at Wakamatsu, Japan [1], was developed. In wet processes, heat loss by water condensation is considerably large compared with dry processes and a plant for waste liquid treatment is also needed, which brings the considerable loss in efficiency in a gloss system. In addition, COS cannot be removed directly by wet processes, so that a COS converter is needed which makes COS to H_2S .

In this work dry desulfurization process is focused and the synthesis of new absorbents which remove sulfur compounds simultaneously as alkali and heavy metals. Calcium, iron, zinc and copper compounds have been used so far as major desulfurization sorbents. Because the optimum temperature for desulfurization by iron oxide is lower than calcium oxide, iron oxide type compounds is most popular sorbents in Japan and operating temperature for desulfurization is set to 673 - 773 K from the aspect to use economical material for reactors and pipelines. For iron system, however, iron carbide is also produced in coal gasification conditions, which brings coking trouble. To avoid this trouble, Shirai et al. [2] developed ultra-fine silica powder mixed iron oxide and zinc ferrite type sorbents and high desulfurization performance without coking and decomposition of zinc ferrite into ferrite and zinc oxide. Dilution of iron oxide or zinc ferrite with third material powder is considered to be advantageous to avoid sintering and coking. If such dilutant has capability to absorb alkali and heavy metals, which also need to be removed, such composite sorbents expected to have both desulfurization and metal absorption capacity. The candidate materials focused at the present research and having the capability of alkali and heavy metals are kaolinite [3], alophen, sepiolite and activated clay.

In our series of research two methods to make composite particles having the capability of both sulfur and metal absorber have been attempted, i.e., dry physical/mechanical method and wet liquid phase chemical synthesis. In dry mechanical method, desulfurization sorbent particles and metal absorption particles were mixed with a ellipsoidal type mixer and core metal absorbers were successfully covered with iron oxide or zinc ferrite layers. The composite particles such obtained have sufficient ability to absorb alkali [4], however, the desulfurizer component in composite sorbent was not sufficiently high as expected high desulfurization performance.

The objective of the present research is the synthesis such composite sorbents by wet liquid phase Process. Alkali and heavy metal absorber, such as kaolinite, sepiolite and activated clay, was added into the reactant solution for iron oxide or zinc ferrite preparation by precipitation and ripening process, referring to so-called gel-sol process [5]. Zinc ferrite can be synthesized by coprecipitation and calcination instead of long term ripening. Sorbents synthesized was tested its desulfurization performance by H₂S removal from model gas. Target H₂S concentration after desulfurization is set to 20 ppm in the present work. Excess H₂S need to be reduced for acceptable gasification gas into fuel cell units is planed to be removed by an additional precise desulfurization units to 1 ppm level.

EXPERIMENTAL

Sorbent Synthesis and Characterization

Sorbents were synthesized two different patterns and here we call them Pattern 1 and Pattern 2. Table 1 summarizes composition of starting solution. Samples 1 to 4 in Table 1 were made by Pattern 1 and Samples 5 to 10 by Pattern 2.

In Pattern 1, into the solution A stirred at 500 rpm, Solution B is added over 5 min at room temperature. After addition, the solution was stirred at 800 rpm for 10 min and ripened for 10 days at 100°C in a capped bottle. The slurry was cooled by running water from the outside of the bottle under atmospheric pressure, washed by distilled water and separated by centrifuge. Washing and centrifugal separation was repeated for three times and purified slurry was dried at 80°C for 24 h to obtain final powdery products.

In Pattern 2, into the solution A stirred at 500 rpm at 313 K, solution B is added over 5 min and stirred at 500 rpm for 1 h. The obtained slurry was washed and centrifugal separated twice and dried at 100°C for 1 h. This powder was calcined at 800°C for 5h.

Prepared powder was observed by FESEM and characterized its crystal by XRD. Specific surface area was measured by BET.

Table 1 Sorbent Preparation Conditions

| Sample | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|------------|----------------------------------|------------------|--|------------------|--|----------------------|---|--|----------------------|----|
| Solution A | 2.0M FeCl ₃ 100 ml | | 1.5M Fe(NO ₃) ₃ 100 ml | | 1.5M Fe(NO ₃) ₃ 100 ml | | | 1.5M Fe(NO ₃) ₃ 70 ml 1.5M Zn(NO ₃) ₂ 35 ml | | |
| | - | - | - | - | Sepio- lite 4 g | Activated clay 4g | - | Sepio- lite 4 g | Activated clay 4g | |
| Solution B | 6M NaOH 100 ml | | 4.5M NH ₃ 100ml | | 4.5M NH ₃ 100 ml | | | | | |
| | - | Kaolinite 5 g | - | Kaolinite 4 g | | | | | | |

Desulfurization Test

Figure 1 shows a desulfurization test apparatus. A reactor is made by coaxial quartz glass tubes having inner diameters of 35 mm for an outer tube and 20 mm for an inner tube. 1 g sorbent sample is set above the 20 mm thickness ceramic filter made of cordierite. After furnace temperature reached 400°C under nitrogen atmosphere flowing at 2 l/min, gas was switch to mixed gas having composition of 4% H_2 - N_2 balance for 30 min to reduce sorbent preliminarily. Desulfurization was performed introducing gas having 1000 ppm H_2S - 2% H_2 - N_2 balance at 2 l/min into the reactor. Exit gas from the furnace was kept over 100°C by ribbon heaters and lead to FTIR (Nexus470, Thermo Electron) and H_2S concentration was monitored until detected H_2S concentration almost returned to the inlet value. After desulfurization test, sorbent was characterized by FESEM and XRD.

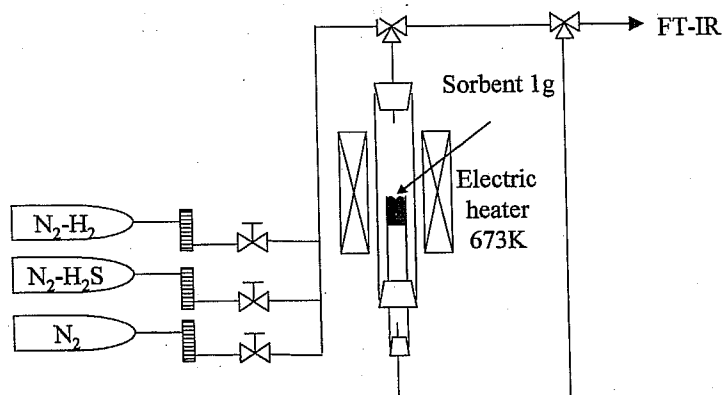


Figure 1 Apparatus for desulfurization testing.

RESULTS AND DISCUSSION

Figure 2 shows FESEM images for synthesized sorbents. Numerals in parentheses indicate their specific surface areas in m^2/g . The upper four images are results from the synthesis without adding metal-absorber particles. Images for metal-absorber particles added, to the reactant solution, kaolinite, sepiolite and activated clay, are also shown in this figure.

For all four types, i.e., iron oxide made by Pattern 1, NaOH precipitation-ripening (left), iron oxide made by Pattern 1, NH_3 precipitation-ripening (left second), iron oxide made by Pattern 2, precipitation-calcination (middle column) and zinc ferrite made by Pattern 2, coprecipitation-calcination (right second), addition of metal-absorber particles made resulted sorbents finer and their specific surface area large. Sorbents with higher surface areas were obtained for Pattern 1 (precipitation-ripening) method than those for Pattern 2 (precipitation-calcination) method.

In XRD charts for iron oxide type sorbents, the peaks of hematite were detected in composite powders (Samples 2, 4, 6, 7) though their intensities were weakened. On the contrary the peaks from metal-absorber particles can not be seen in these composite powders, Samples 2, 4, 6. In Sample 7 slight peak from activated clay can be detected. For zinc ferrite systems peaks from franklinite were detected for all three Samples 8, 9, 10 and weak peaks from activated clay remained in composite powder (Sample 10).

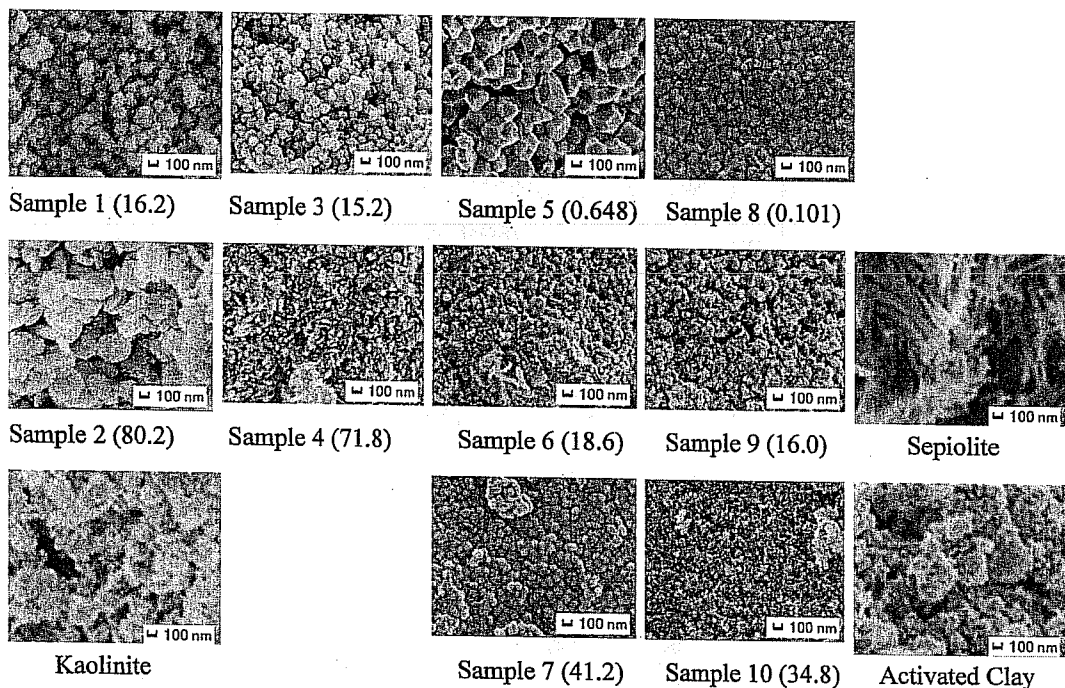


Figure 2 SEM image of synthesized sorbents and metal absorption particles
 Numerals in parentheses are specific surface area, unit: m^2/g

Figure 3 shows the results from desulfurization tests. Samples used are six composite sorbents. Two samples made by Pattern 1 method decreased exit H_2S once less than 10 ppm and as sorbents consumed exit H_2S increased gradually. From the time profile of exit H_2S concentration, conversion of sorbent was calculated and shown in Figure 4. Almost all iron reacted effectively with H_2S for sorbents made by Pattern 1 (precipitation-ripening) method.

The iron oxide type samples made by Pattern 2 (precipitation-calcination) method having lower specific surface area had conversion less than 50 %. A zinc ferrite type sample had a little higher conversion. Conversion is indicated with the function of specific surface area as shown Figure 5. Conversion was almost proportional to specific surface area, and zinc ferrite type composite particles had a little higher conversion than iron oxide type ones.

Figures 6 and 7 show SEM image and XRD patterns of Pattern 1 method composite sorbents before and after desulfurization, whose conversion was the second highest or highest. No remarkable sintering was observed from samples after desulfurization. The peaks for hematite were decreased after desulfurization for both samples. These peaks almost disappeared for Sample 4 whose conversion was highest of all six samples tested. Peaks for pyrrhotite were detected from both samples after desulfurization. Absorption of sodium was also tested for Sample 4 and absorption ratio was as high as that of composite particles prepared by dry physical/mechanical method, which will be reported in our separate paper.

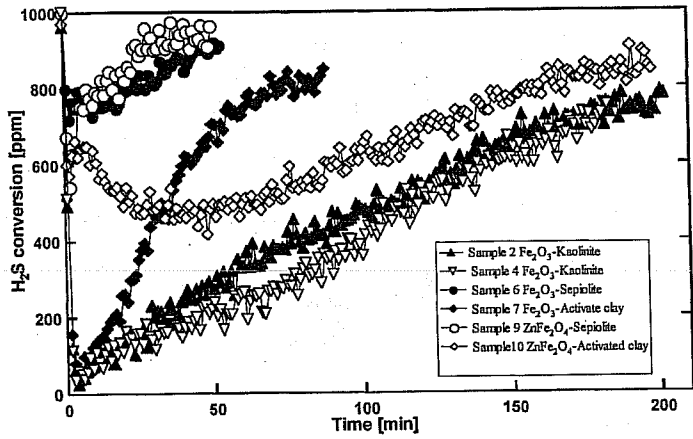


Figure 3 Exit H₂S concentration for desulfurization test

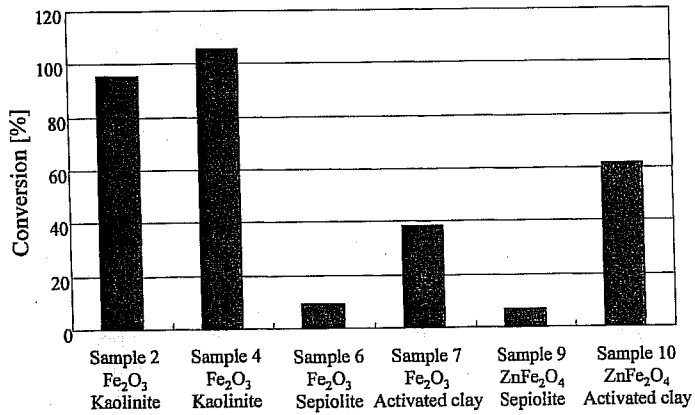


Figure 4 Conversion of Fe₂O₃ or ZnFe₂O₄

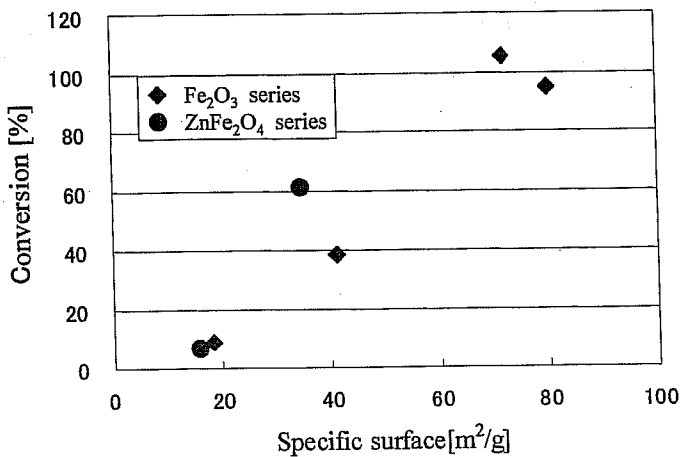
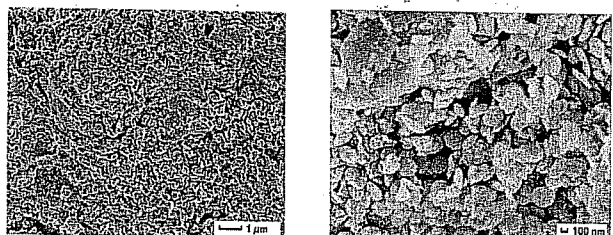


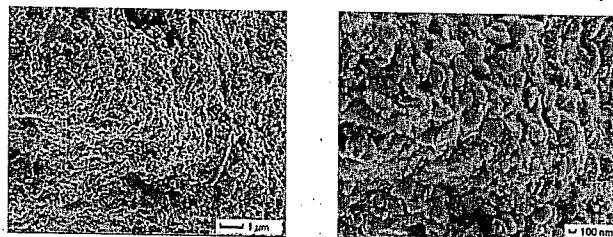
Figure 5 Relation between specific surface area and conversion

CONCLUSION

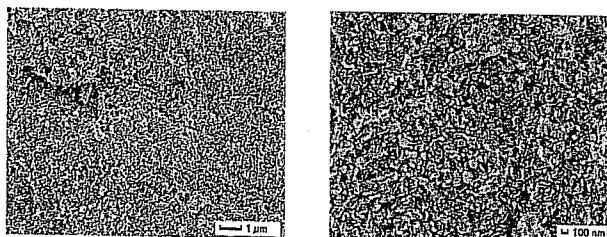
Iron oxide and zinc ferrite type desulfurization sorbents composing metal-absorbent particles were synthesized by precipitation-ripening method and precipitation-calcination method. Sorbents with metal-absorbent particles were finer than those without them and specific surface area was enlarged. Sample made by precipitation-ripening method had remarkably high specific surface area. Desulfurization capacity to remove H_2S from 1000 ppm H_2S - 2% H_2 - N_2 balance model gas was increased with increasing the specific surface area of composite sorbent.



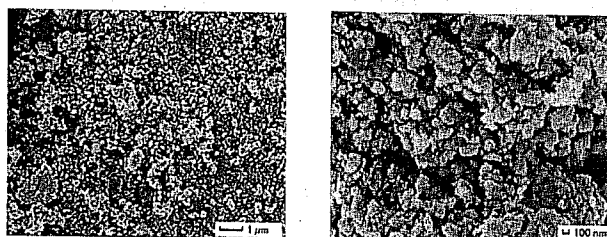
(a) Before desulfurization (Sample 2 Fe_2O_3 -kaolinate)



(b) After desulfurization (Sample 2 Fe_2O_3 -kaolinate)

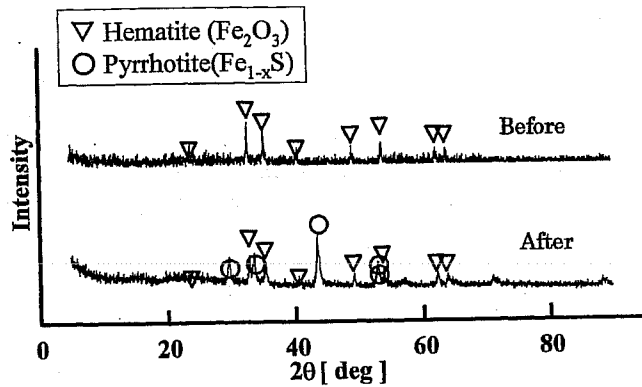


(c) Before desulfurization (Sample 4 Fe_2O_3 -kaolinate)

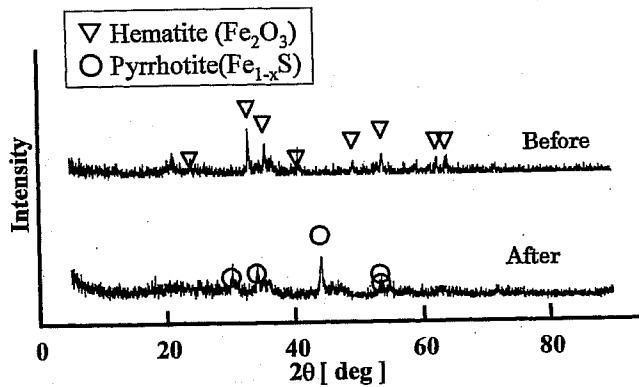


(d) After desulfurization (Sample 4 Fe_2O_3 -kaolinate)

Figure 6 FESEM image of sorbents before and after desulfurization.



(a) Sample 2 Fe_2O_3 -kaolinate



(b) Sample 4 Fe_2O_3 -kaolinate

Figure 7 XRD pattern of sorbent particles before and after desulfurization

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REFERENCES

1. Sotooka, M. "Coal Gasification Technology (II) — Coal Energy Application for Gas, Liquid & Electricity (EAGLE), *J. Japan Inst. Energy*, 82, 836-840 (2003)
2. H. Shirai, M. Kobayashi, M. Nunokawa, Characteristics of H_2S Removal of Mixed-oxide Sorbents Containing Fe and Zn at High Temperatures, *J. Japan Inst. Energy*, 77, 1100-1110 (1998)
3. Trun, S. Q. C. M. Kinoshita, D. M. Ishimura, J. Zhou, T. T. Hiraki, S. M. Masutani, "A review of sorbent materials for fixed bed., *J. Inst. Energy*, 71, 163-177 (1998)
4. M. Mizutani, S. Kambara, H. Moritomi, M. Tsukada, H. Kamiya, K. Abe, Y. Yonemichi, T. Alkali "Components and Heavy Metal Removal by Composite Particles", *Preprints of 70th Annual Meeting of Soc. Chem. Eng. Japan*, K318 (2005)
5. Sugimoto, T., K. Sakata, A. Muramatsu, "Formation Mechanism of Monodisperse Pseudocubic $\alpha\text{-Fe}_2\text{O}_3$ Particles from Condensed Ferric Hydroxide Gel", *J. Colloid Interface Sci.*, 159, 372-382, (1993)