

Development of BaTiO₃-based catalyst for tar reforming

Main author

T.Haneda
TOKYO GAS CO.,Ltd
Japan
haneda@tokyo-gas.co.jp

Co-author

Y.Yokoi
T.Matsui

1. ABSTRACT

Gasification is an efficient and environmentally friendly way to produce energy from biomass. The gasification technology has a serious problem for the use of gasses that contain tar. The presence of tar can cause blockage and corrosion of some pipes, filters, and heat exchangers in the gasification system. Catalytic removal of tar has been found to be an effective way to convert tar into valuable gasses. However, one of the problems in the use of catalysts is that the biomass gasification gasses generally contain high amounts of H₂S, in the range of 100 to 2000 ppm. For this reason, the sulphur tolerance of the catalyst is very important because it is well known that the catalyst is easily deactivated by H₂S. Therefore, we have been developing a tar removal catalyst with a high sulphur tolerance. In our previous studies, we found that Fe-Sr/BaTiO₃ shows high activity as a tar removal catalyst in simulated gasification gasses. In addition, we found out special property of BaTiO₃-based catalyst that H₂S worked as a promoter of steam reforming.

In this study, we investigated the effects of H₂S on a Fe-Sr/BaTiO₃ catalyst in a tar reforming reaction by studying the reformation of methane and toluene under these conditions. Moreover, we investigated the long-term stability of the Fe-Sr/BaTiO₃ catalyst against H₂S by testing with simulated gasification gases for 100 h.

Consequently, the addition of H₂S clearly improved tar reforming activity, which consists of C–H bonds and C–C bond, on Fe-Sr/BaTiO₃ at 750 °C, were based on the results of our demonstration test for the gasification of sewage sludge. Moreover, the addition of H₂S clearly prevented the formation of carbon on the Fe-Sr/BaTiO₃ catalyst, whereas the addition of H₂S promoted the formation of carbon on Ni/Al₂O₃. These results can be applied to the study of the mechanism of tar reformation on a Fe-Sr/BaTiO₃ catalyst, which will subsequently lead to an improvement in the reforming activity of this catalyst. We anticipate that the unique catalyst developed in this study will enable more use of biomass gasification systems and thereby contribute to the establishment of a low-carbon society.

TABLE OF CONTENTS

1. Abstract

2. Body of Paper

2.1 Introduction

2.2 Experimental

2.3 Results and discussions

2.4 Conclusions

3. References

4. List of Figures

2. BODY OF PAPER

2.1 Introduction

Gasification is an efficient and environmentally friendly way to produce energy from biomass. In the gasification of biomass, gases can be burned to produce heat, supplied to gas engines or fuel cells to produce electricity, or upgraded to synthesized gas. We previously developed a gasification system that produced energy from sewage sludge and supplied the resultant gasification gas to gas engines¹⁾ (Fig.1). The technology associated with gasification is, however, seriously challenged by the use of gases that contain tar. Tar is gaseous at high temperatures, but it may condense at low temperatures. For this reason, the presence of tar can cause the blockage and corrosion of some pipes, filters, and heat exchangers in the gasification system (Fig.2). An effective way to convert tar into valuable gases is via the removal of tar using a catalytic process. However, one of the problems in the use of such catalysts is that the gases produced from biomass gasification generally contain high concentrations of H₂S, in the range of 100 to 2000 ppm. Given that the catalyst is easily deactivated by H₂S, the tolerance of the catalyst to sulfur is critical in this process. We have therefore been developing a catalyst for tar removal that has a high sulfur tolerance.



Fig.1 Gasification system for sewage sludge



Fig.2 View of pipe blocked by tar

In our previous studies, we found that Fe-Sr/BaTiO₃ shows high activity as a tar removal catalyst in simulated gasification gases (H₂, CO, CH₄, CO₂, H₂O, N₂, and C₇H₈) containing H₂S in a concentration greater than 500 ppm²⁾. Moreover, we discovered that H₂S worked as a promoter in the reaction for the reformation of tar steam when using a BaTiO₃-based catalyst. In addition, BaTiO₃ is used extensively as a material for ceramic capacitors, so the material cost is less than that for Ni-based catalysts. Moreover, if the waste BaTiO₃ released from the capacitor industry can be used in a BaTiO₃-based catalyst in the future, the cost of the catalyst would reduce even further. We therefore conclude that a BaTiO₃-based catalyst has great potential for application in tar removal in the gasification of biomass.

The main purpose of this study is to evaluate the effects of H₂S on Fe-Sr/BaTiO₃ in the tar steam reforming reaction. Tar is a mixture of several different compounds that mostly have C–H and C–C bonds. Therefore, the ideal catalyst for tar reformation needs to activate both C–H and C–C bonds. In this study, the Fe-Sr/BaTiO₃ catalyst was first evaluated in a methane (CH₄) reforming reaction, which consists of C–H bonds, in order to confirm the effects of H₂S on C–H bond activation. Then, Fe-Sr/BaTiO₃ was evaluated in a toluene (C₇H₈) reforming reaction, which mainly consists of C–C bonds, in order to confirm the effects of H₂S on C–C bond activation. Finally, in order to confirm the practical use of this catalyst, Fe-Sr/BaTiO₃ was evaluated in terms of its long-term stability against

H₂S by combination with simulated gasification gases for 100 h.

2.2 Experimental

2.2.1 Preparation and characterization of the catalyst

The Fe-Sr/BaTiO₃ catalyst used in this study was prepared by a solid-phase process. BaTiO₃, with high activity as steam reforming catalyst, was selected in the form of a ceramic capacitor material that was available in the market. Fe₂O₃ and SrCO₃ (1.0 wt% each) were then added to the BaTiO₃ (Brunauer–Emmett–Teller (BET) specific surface area = 20–22 m²/g, Ba:Ti = 0.99:1.01) and mixed in a mortar for 20 h. The catalysts were calcined at 750 °C in air for 1 h. According to the transmission electron microscopy (TEM) image (Fig.3), the size of the BaTiO₃ particles was found to be 30–50 nm. Moreover, energy dispersive X-ray spectroscopy (EDX) illuminated a part of Fe and Sr around the surface of the BaTiO₃ particles. According to the X-ray diffraction (XRD) pattern (Fig.4), Fe-Sr/BaTiO₃ has a perovskite structure with a small amount of BaCO₃, but the peaks of Fe and Sr could not be confirmed. The specific surface area of Fe-Sr/BaTiO₃ was determined as 21 m²/g by BET measurement.

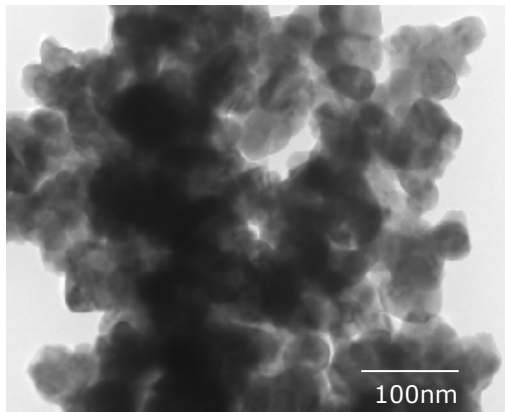


Fig. 3 TEM micrograph of Fe-Sr/BaTiO₃

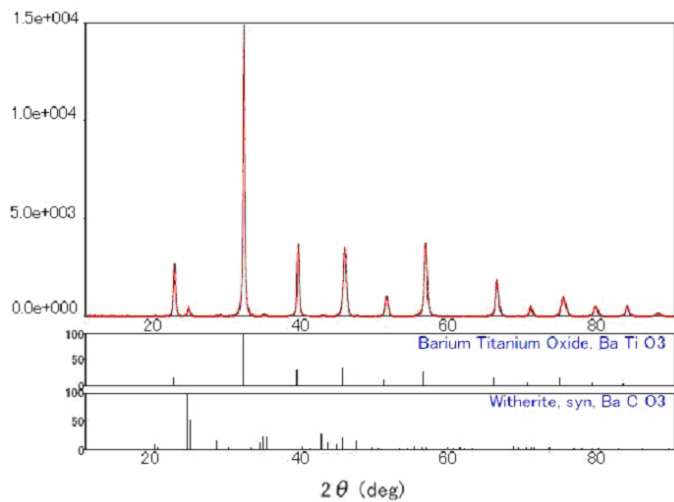


Fig. 4 XRD pattern of Fe-Sr/BaTiO₃

2.2.2 Activity tests

All of the tests in this study were carried out in a fixed-bed reactor at atmospheric pressure. A quartz tube was set up in an electric oven, and the oven temperature was controlled in the range of 0–900 °C. The diameter and length of the tube were 20 mm and 500 mm, respectively. The temperature at the bottom of the catalyst bed was adjusted to be the set point temperature. A quartz grid and a thermocouple pocket built inside the reactor were used to measure the temperatures of the catalyst bed. A K-type thermo element with an outer diameter of 1 mm was inserted into the thermo-couple pocket.

2.2.2.1 Methane reforming test

The methane reforming test was carried out at 750–850 °C. The experimental gases were mixed in a composition of 20% CH₄, 20% H₂O (S/C = 1.0), 0–2000 ppm H₂S, and N₂ (balance) using mass flow controllers. The space velocity (SV) in the experiments was 5000 h⁻¹.

2.2.2.2 Toluene reforming test

The toluene reforming test was carried out at 650–850 °C. The experimental gases were mixed in compositions of 20% H₂O (S/C = 4.5), 6400 ppm C₇H₈ (simulated tar), 0–2000 ppm H₂S, and N₂ (balance) using mass flow controllers. The SV in the experiments was 10000 h⁻¹.

The toluene conversion, toluene decomposition ratio, and hydrogen yield were calculated using the formulae given below. The toluene conversion, denoted as X_c (Eq.(1)), is the ratio of carbon converted into carbon-containing gaseous products (CO , CO_2 , CH_4 , and C_6H_6) to carbon present in toluene. The toluene decomposition ratio, denoted as X_d (Eq.(2)), is the ratio of decomposition of toluene to that of benzene, because toluene is demethylated to benzene at high temperatures. The hydrogen yield, denoted as Y_{H_2} (Eq.(3)), is expressed as the percentage of stoichiometric potential that corresponds to the total conversion of toluene into H_2 and CO by toluene steam reforming with excess water.

$$X_c = ([\text{CO}]_{\text{out}} + [\text{CO}_2]_{\text{out}} + [\text{CH}_4]_{\text{out}} + 6[\text{C}_6\text{H}_6]_{\text{out}}) / 7[\text{C}_7\text{H}_8]_{\text{in}} \times 100 \quad (1)$$

$$\left(\doteq ([\text{C}_7\text{H}_8]_{\text{in}} - [\text{C}_7\text{H}_8]_{\text{out}}) / [\text{C}_7\text{H}_8]_{\text{in}} \times 100 \right)$$

$$X_d = ([\text{CO}]_{\text{out}} + [\text{CO}_2]_{\text{out}} + [\text{CH}_4]_{\text{out}}) / 7[\text{C}_7\text{H}_8]_{\text{in}} \times 100 \quad (2)$$

$$\left(\doteq ([\text{C}_7\text{H}_8]_{\text{in}} - [\text{C}_7\text{H}_8]_{\text{out}} - [\text{C}_6\text{H}_6]_{\text{out}}) / [\text{C}_7\text{H}_8]_{\text{in}} \times 100 \right)$$

$$Y_{\text{H}_2} = [\text{H}_2]_{\text{out}} / 11[\text{C}_7\text{H}_8]_{\text{in}} \quad (3)$$

2.2.2.3 Long-term stability test

The chosen conditions for the long-term test with simulated gasification gases, carried out at 750°C , were based on the results of the demonstration test for the gasification of sewage sludge²⁾. The simulated gasification gases were mixed in a composition of 8% H_2 , 8% CO , 2.5% CH_4 , 14% CO_2 , 20% H_2O , 500 ppm H_2S , 6400 ppm C_7H_8 (simulated tar) and N_2 (balance). The SV in the experiments was 10000 h^{-1} , and the test run time was 100 h. It is worth noting that benzene (C_6H_6) is not classified as tar³⁾ and is a known persistent component of naphthalene (C_{10}H_8), which is the main structural material in biomass tar⁴⁾. The conversion of tar in this experiment is therefore denoted as X_c (Eq.(1)).

2.2.3 Analysis methods

The resultant gases were analyzed using an online gas chromatograph equipped with TCD and FID. Following the reaction, the amount of coke deposited on the catalyst was investigated by using an elemental analyzer.

2.3 Results and discussions

2.3.1 Methane reforming test

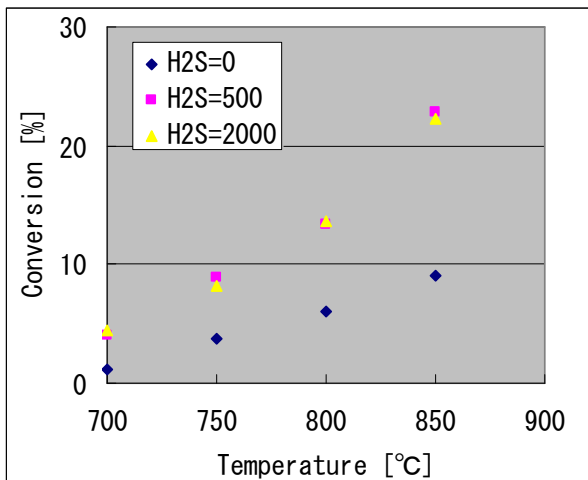


Fig. 5 Methane conversion as a function of temperature

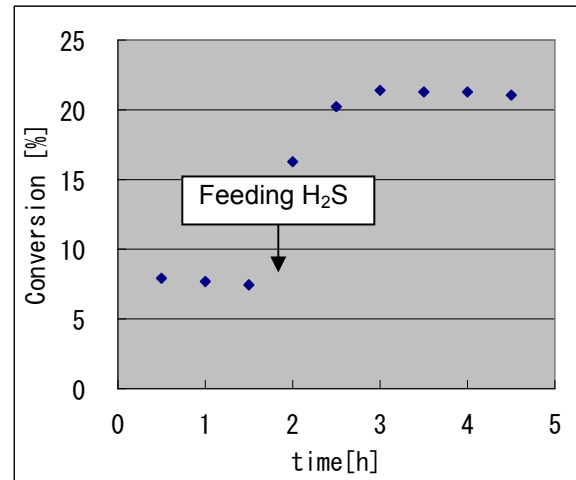


Fig. 6 Methane conversion as a function of time at 850°C

In this study, H₂S concentrations of 0,500 and 2000 ppm were added to the reaction at 750–850 °C with a CH₄/H₂O ratio of 1.0. As shown in Fig.5, we found that the presence of H₂S increased the conversion of methane. In the absence of H₂S, less than 10% of the methane was converted at 850 °C. When H₂S was added, over 20% of the methane was converted at 850°C. Moreover, the temporal change of methane conversion during the reaction at 850 °C was investigated by addition of 500 ppm H₂S after the reforming test had occurred for 1.5 h without H₂S. As shown in Fig.6, we found that the methane conversion increased from under 10% to over 20% upon addition of H₂S along with CH₄ and H₂O. These results clearly indicate that H₂S works as an activator for the methane reforming reaction on a Fe-Sr/BaTiO₃ catalyst. As a result, we propose that H₂S works as an activator for the C–H bond activation.

2.3.2 Toluene reforming test

In order to evaluate the activation of C–C bonds in this process, the effect of H₂S on the reforming activity of toluene steam in the presence of Fe-Sr/BaTiO₃ was investigated at 650–850 °C. The toluene conversion (Fig.3), toluene decomposition ratio (Fig.4), and H₂ yield (Fig.5) all increased with an increase in temperature at all H₂S concentrations. However, the variations in the toluene conversion, toluene decomposition ratio, and H₂ yield were dissimilar. The addition of H₂S clearly improved the toluene conversion and toluene decomposition ratio at 650–750 °C.

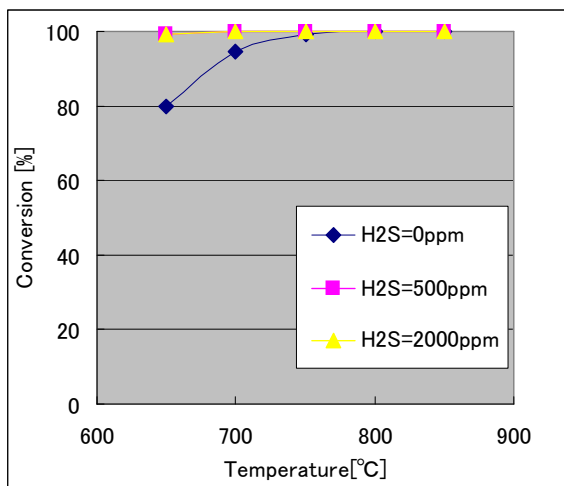


Fig.7 Toluene conversion as a function of temperature

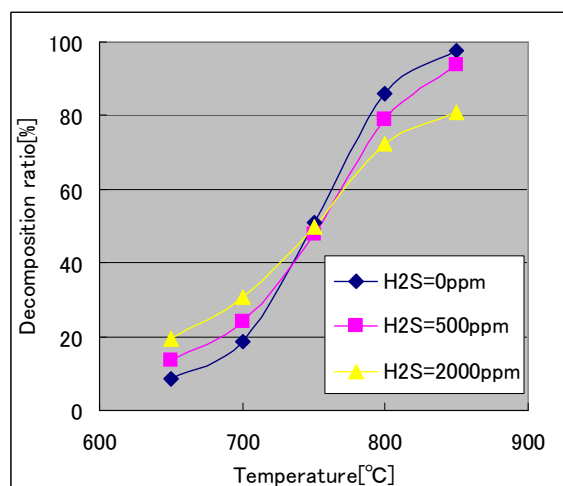


Fig.8 Toluene decomposition rate as a function of temperature

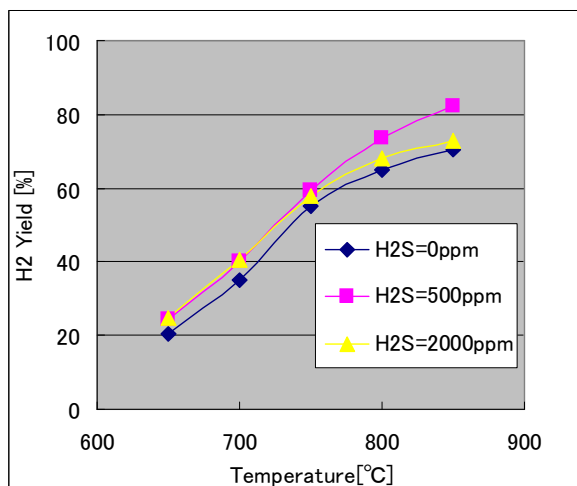


Fig.9 H₂ yield as a function of temperature

However, the toluene decomposition ratio in the case of H₂S addition at 750–850 °C was slightly lower than that without this addition. These results indicate that H₂S works as an activator for the reforming reaction of toluene on Fe-Sr/BaTiO₃ catalyst at low temperatures (650–750 °C), but it works as a deactivator for this reaction at high temperatures (750–850 °C).

Moreover, the addition of H₂S had a mildly positive effect on the H₂ yield at all temperatures. This indicates that H₂S reacts with water to form SO₂ and H₂ at higher temperatures⁵⁾. However, although we hypothesized that H₂S has an enhancing effect on the catalytic activity of Fe-Sr/BaTiO₃, the formation of SO₂ instead of H₂S indicates a decrease in the reforming activity of Fe-Sr/BaTiO₃. In addition, the low toluene decomposition ratio explains the high generation of benzene in the results because the toluene conversion is sufficiently high under all conditions in the experiment. We therefore propose that H₂S works as an activator for C–C bond activation at low temperatures, whereas SO₂ works as a deactivator for C–C bond activation at high temperatures.

2.3.3 Long-term stability test

The Fe-Sr/BaTiO₃ catalyst was evaluated for its long-term stability against H₂S by testing in combination with simulated gasification gases at 750 °C. The toluene conversion was measured as a function of time in order to indicate both the stability and the degree of deactivation. For comparison, the long-term stability in the toluene reforming process on both a commercial steam reforming catalyst (Ni (20 wt%)/Al₂O₃) and the synthesized Fe-Sr/BaTiO₃ catalyst without H₂S was also evaluated. In general, metal-based catalysts such as Ni and Pd are deactivated by sulfur in order to accelerate the formation of carbon with increasing Bronsted acidity on metal⁶⁾. Fig.10 shows a comparison of the activity among Fe-Sr/BaTiO₃ with 500 ppm H₂S, Fe-Sr/BaTiO₃ without H₂S, and Ni/Al₂O₃ with 500 ppm H₂S, at an SV of 10,000 h⁻¹. It was found that the toluene reforming activity on the Fe-Sr/BaTiO₃ with H₂S was greater than Ni/Al₂O₃ with H₂S. Significant deactivations were detected for Ni/Al₂O₃ with H₂S, whereas much lower deactivations were observed on Fe-Sr/BaTiO₃ with H₂S. Moreover, it was found that the toluene reforming activity on Fe-Sr/BaTiO₃ with H₂S was greater than that on Fe-Sr/BaTiO₃ without H₂S, although H₂S hardly influenced the initial activity on Fe-Sr/BaTiO₃ in the toluene reforming test at 750 °C. It should be noted that an elemental analyzer was used to determine whether the observed deactivation was due to the carbon formation derived by sulfur.

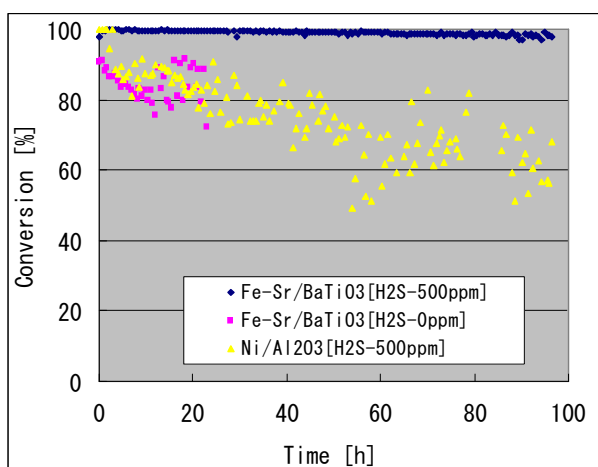


Fig.10 Comparison of toluene reforming activity between Fe-Sr/BaTiO₃ and Ni/Al₂O₃ at 750°C

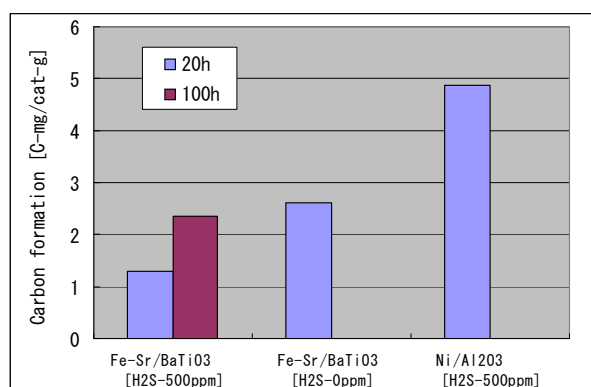


Fig.11 Comparison of carbon formation between Fe-Sr/BaTiO₃ and Ni/Al₂O₃

The results obtained using the elemental analyzer, shown in Fig.11, indicate the formation of large amounts of carbon in the cases of Ni/Al₂O₃ with H₂S and Fe-Sr/BaTiO₃ without H₂S, but a significantly lower amount of carbon formed in the case of Fe-Sr/BaTiO₃ with H₂S. These results

clearly indicate that the deactivations observed for Ni/Al₂O₃ with H₂S and for Fe-Sr/BaTiO₃ without H₂S were mainly due to the formation of carbon on the surface of the catalyst. In addition, we guess that the carbon formation is mainly derived sulfur poison on Ni/Al₂O₃. On the other hand, we deduce that the formation of carbon is prevented by H₂S on the Fe-Sr/BaTiO₃ catalyst.

In conclusion, the Fe-Sr/BaTiO₃ catalyst in the presence of H₂S showed a significantly stronger resistance to sulfur poison and carbon formation than to Ni/Al₂O₃.

2.4 Conclusions

We investigated the effects of H₂S on a Fe-Sr/BaTiO₃ catalyst in a tar reforming reaction by studying the reformation of methane and toluene under these conditions. Moreover, we investigated the long-term stability of the Fe-Sr/BaTiO₃ catalyst against H₂S by testing with simulated gasification gases for 100 h. On the basis of our results, we draw the following conclusions:

- (1) The addition of H₂S clearly improved the methane reforming activity, which consists of C–H bonds, on Fe-Sr/BaTiO₃.
- (2) The addition of H₂S clearly improved the toluene reforming activity, which consists of C–C bonds, on Fe-Sr/BaTiO₃ at low temperatures (650–750 °C), whereas H₂S addition caused a slight decrease in the toluene reforming activity of Fe-Sr/BaTiO₃ at high temperatures (750–850 °C).
- (3) The addition of H₂S clearly improved tar reforming activity, which consists of C–H bonds and C–C bond, on Fe-Sr/BaTiO₃ at 750 °C, were based on the results of the demonstration test for the gasification of sewage sludge ¹⁾.
- (4) The addition of H₂S clearly prevented the formation of carbon on the Fe-Sr/BaTiO₃ catalyst, whereas the addition of H₂S promoted the formation of carbon on Ni/Al₂O₃.

These results can be applied to the study of the mechanism of tar reformation on a Fe-Sr/BaTiO₃ catalyst, which will subsequently lead to an improvement in the reforming activity of this catalyst. We anticipate that the unique catalyst developed in this study will enable more use of biomass gasification systems and thereby contribute to the establishment of a low-carbon society.

3. REFERENCES

- 1) T. Haneda, R. Takeya. The development of gasification system for sewage sludge – Report No.3, Proceedings of 17th European Biomass Conference and Exhibition, Hamburg, Germany, 2009.
- 2) T. Haneda, T. Matsui. Development of tar removal catalyst for sewage sludge gasification, Proceedings of 9th *Novel Gas Conversion Symposium*, Lyon, France, 2010.
- 3) H.Ronkkonen, P.Simell, M.Reinikainen, The Effect of Sulfur on ZrO₂-Based Biomass Gasification Gas Clean-Up Catalysts, *Topics in Catalysis*, Vol. 52, 8, 2009.
- 4) A. Jess, Mechanisms and kinetics of thermal reactions of aromatic hydrocarbons from pyrolysis of solid fuels, *Fuel*, Vol.75, 12, 1996.
- 5) H.Aramaki, M.Ikeda, Y. Shirai, Evaluation of the Characteristics of Hydrogen Sulfide Formation in Pulverized Coal Combustion -The influence of Coal Properties on Hydrogen sulfide Formation-, Energy Engineer research Laboratory Report, No. M09010, 2010.
- 6) D.D.Beck, J.W.Sommers, Impact of sulfur on three-way catalyst: comparison of commercially produced Pd and Pt-Rh monoliths, *Studies in Surface Science and Catalysis*, Vol.96, 721, 1995.

4. LIST OF FIGURES

Fig. 1 Gasification system for sewage sludge

Fig. 2 View of pipe blocked by tar

Fig. 3 TEM micrograph of Fe-Sr/BaTiO₃

Fig. 4 XRD pattern of Fe-Sr/BaTiO₃

Fig. 5 Methane conversion as a function of temperature

Fig. 6 Methane conversion as a function of time at 850 °C

Fig. 7 Toluene conversion as a function of temperature

Fig. 8 Toluene decomposition rate as a function of temperature

Fig. 9 H₂ yield as a function of temperature

Fig. 10 Comparison of toluene reforming activity between Fe-Sr/BaTiO₃ and Ni/Al₂O₃ at 750°C

Fig. 11 Comparison of carbon formation between Fe-Sr/BaTiO₃ and Ni/Al₂O₃