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Development of Desulfurization Adsorbent for City Gas for Residential PEFC Cogeneration System

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1. Abstract

Outline

Tokyo Gas has developed new desulfurizers for a fuel processing system of the residential fuel cell, ENE-FARM™. Sulfur compounds in city gas have to be removed before introduction to a fuel processor, because they degrade the activity of catalysts used in the fuel processor. We have already developed a high-performance desulfurizer using a zeolite-base material that can easily remove trace amount of sulfur compounds, and optimized the desulfurizing agent to adapt it to the gas odorant (TBM : tertiary-butylmercaptan) and other sulfur compounds included in the city gas supplied by Tokyo Gas. Recently, we have been concentrating on reducing the cost of the desulfurizer and modified it. Our new idea is replacing some part of the expensive desulfurizing agent with low-cost composites comprised of oxides and activated carbons and it can reduce the desulfurizer cost.

Configuration of the novel desulfurizer

The concept of the new desulfurizer is how to adsorb TBM and how reduce the amount of the precious zeolite. The new desulfurizer can increase the adsorption performance of TBM through its dimerization reaction. The desulfurizer comprises three kinds of adsorbents: transition metal oxides, activated carbons, and Ag-exchanged zeolite which we conventionally employ. Firstly the metal oxide dimerizes TBM and then the activated carbon adsorbs dimerized TBM. Finally the Ag-exchanged zeolite removes trace amount of sulfur compounds as impurities. Thus this desulfurizer is able to largely reduce the volume of the expensive zeolite.

Cost estimation of the novel desulfurizer

We evaluated the adsorption performance of the present desulfurizer under actual operating conditions and revealed that the combination of metal oxides and the activated carbons can adsorb TBM over 5 times better than the conventional expensive Ag-exchanged zeolite. By applying this novel desulfurizer to ENE-FARM™, it is expected that 80% of the material cost can be reduced.

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2. Body of Papers

2.1. Introduction

2.1.1. The residential PEFC cogeneration system, "ENE-FARM"

ENE-FARM generates electric power by reaction of the oxygen in the air and the hydrogen reformed from city gas in the polymer electrolyte fuel cell (PEFC). It also produces hot water by exhaust heat recovery while it generates electric power. ENE-FARM is capable of saving energy and reducing CO_2 emissions, thus it is expected as the next-generation electric generating system.

Tokyo Gas started to sell the first commercial model of ENE-FARM in 2009 and released the second generation model, the previous model, in 2011. It has developed the new model of ENE-FARM jointly with Panasonic Corporation and launched it in April, 2013 (Figure 1). Approximately 30,000 systems in total were sold by the end of April 2014.

Figure 1 Appearance of the new model of ENE-FARM

2.1.2. Desulfurization for ENE-FARM

City gas is known as a clean fuel because it has fewer sulfur compounds than the other fossil fuels. However, small amounts of odorant consisting of mainly sulfur compounds are added to city gas for warning of gas leakage. As the catalysts of a fuel processing system and fuel cell electrodes are poisoned by sulfur compounds, it must be previously desulfurized with the desulfurizer in the system[1, 2)].

Tokyo gas had used *tertiary*-butyl mercaptan (TBM) and dimethyl sulfide (DMS) as odorants before. However, by 2010, we have achieved a further reduction of the volume of sulfur compounds in city gas by means of replacing DMS with cyclohexene (C_6H_{10}) which does not contain sulfur. LPG added in order to adjust city gas to the prescribed calorific value contains trace amounts of impurity sulfurs such as methyl mercaptan (MM), hydrogen sulfide (H_2S), tetrahydrothiophene (THT), and carbonyl sulfide (COS). The desulfurizer loaded in ENE-FARM must remove all the sulfur compounds contained in city gas.

The hydrodesulfurization and the adsorptive desulfurization at ambient temperature are known for desulfurization methods of city gas. We consider that the adsorptive desulfurization at ambient air temperature fits ENE-FARM that requires simple operation. Thus, we have focused on the development of the adsorptive desulfurizing agents at ambient temperature.

2.1.3. Development of sulfurizing agents for ENE-FARM in Tokyo gas

We have already developed a high-performance desulfurizer using the Ag-exchanged Y-type zeolites (Ag/Na-Y) that is able to remove all the sulfur compounds in city gas[3)]. It is also found that Ag/Na-Y is not easily influenced by impurities such as moisture in a fuel and can remove sulfur compounds at ambient temperature without any complicate pretreatment. However, for further cost reduction of the system, it needs the development of a low-cost desulfurizer by reducing the volume of the expensive Ag/Na-Y.

It has been recognized that two TBMs form a TBM dimer by being oxidized on transition metal oxides[4)] (Figure 2). Through the reaction above, we suggest the novel desulfurizer consisting of the triple layers (Figure 3) : the first layer; transition metal oxides, the second layer; activated carbons, the third layer; Ag/Na-Y. First the transition metal oxides dimerize TBM and then the activated carbon adsorbs the TBM dimer. Finally Ag/Na-Y removes trace amounts of impurity sulfurs. Thus, this desulfurizer is able to significantly reduce the volume of the expensive Ag/Na-Y. This paper describes a variety of evaluations and cost estimation for the novel desulfurizer consisting of the triple layers.

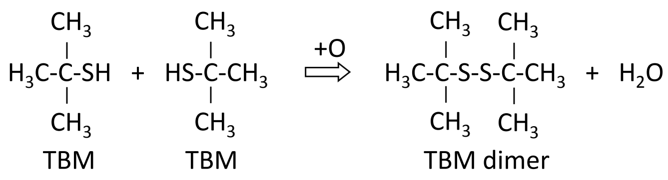

Figure 2 Dimerization reaction of TBM on transition metal oxides

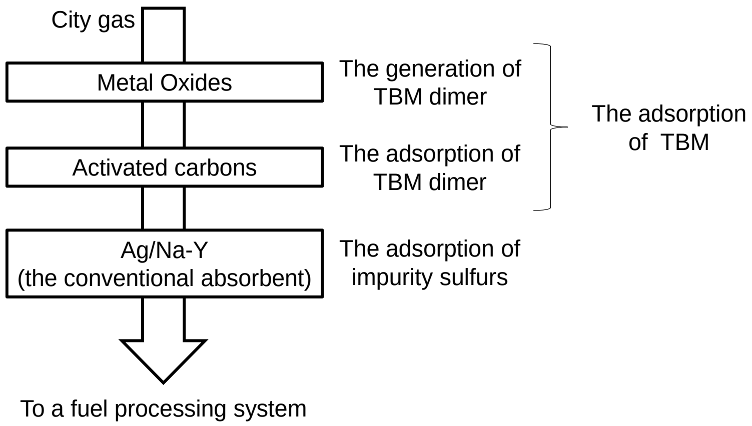

Figure 3 Configuration and adsorption mechanism of the novel desulfurizer

2.2. Experimental

2.2.1. Fixed-bed flow system

Figure 4 shows the schematic diagram of the adsorption test apparatus. The adsorption tests were carried out in a fixed -bed flow reactor (i.d.: 8 mm) containing 1 cm^3 of agents at a normal pressure. The test gas was desulfurized city gas with the addition of sulfur compounds diluted with nitrogen to a small ppm. The water concentration of the test gas was less than 20 ppm at dew point of -60℃ (dry condition) and was adjusted to 500 ~ 12,000 ppm at dew point of -30 ~ 10℃ by bubbling part of the test gas through temperature-controlled water (wet condition). The gas flow rate was 1000 cm^3 min^{-1} and the GHSV was 60,000 hr^{-1}. Concentrations of sulfur compounds in the inlet and outlet gases were analyzed by a gas chromatograph equipped with a packed column of TCEP 25% with H_3PO_4 3% and a flame photometric detector on a SHIMADZU, GC-14B (the lower limit of quantitation of 0.02 ppm).

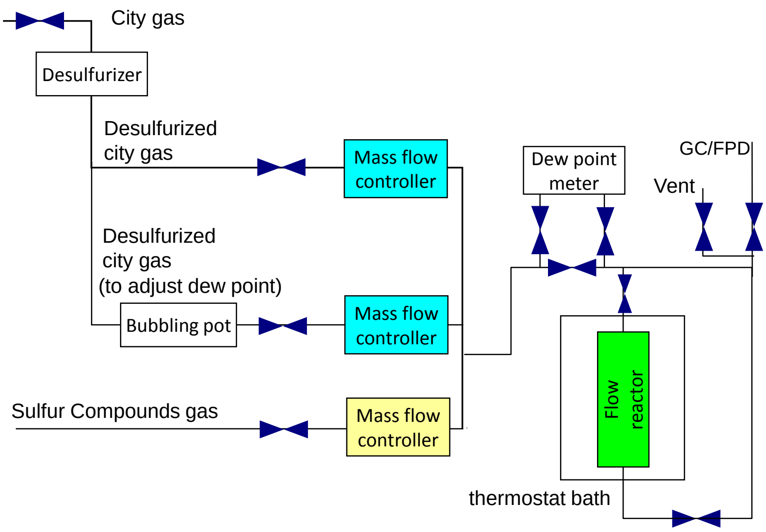

Figure 4 Schematic diagram of the adsorption test apparatus.

2.2.2. Sulfur adsorption experiments

The performance evaluations of transition metal oxides and activated carbons in the novel desulfurizer consisting of the triple layers were conducted under a variety of temperature and dew point. The adsorption tests were carried out a specific combination of temperature at 25, 60℃ and dew point at -60, -30, -15, and 10℃ (20, 500, 1900,and 12000 ppm as water concentration, respectively). 8 ppm TBM and 16 ppm C_6H_{10} were added to the test gas. The capacities of dimerization of TBM on transition metal oxides were calculated from quantity of dimerization of TBM before it broken through in the outlet gas. The adsorption capacities of TBM dimer on activated carbons was also calculated by the same method as mentioned above.

From the results of our preliminary tests, we selected agent A as transition metal oxides and G2x (Japan EnviroChemicals, Ltd.) as activated carbons.

The performance evaluations of impurity sulfurs with Ag/Na-Y were conducted. MM, THT, H_2S, and DMS are used as impurity sulfurs. The adsorption tests were carried out a specific combination of temperature at 25, 60℃ and dew point at -60, -30, -20, and 10℃ (20, 500, 1200,and 12000 ppm as water concentration, respectively). 10 ppm sulfur compounds were added to the test gas. The sulfur adsorption capacities of Ag/Na-Y were calculated from quantity of adsorbed impurity sulfurs before it broken through in the outlet gas.

2.3. Results and Discussion

2.3.1. Adsorption performances of the agents in the novel desulfurizer consisting of the triple layers

First, the results of adsorption performance of TBM on agent A and G2x at a variety of temperature and dew point are shown in Figure 5. The capacity of dimerization of TBM on agent A was over 12 wt%S, the adsorption capacity of TBM dimer on G2x was over 10 wt%S. Agent A and G2x can adsorb TBM over 5 times better than the conventional expensive Ag/Na-Y. In addition, agent A and G2x were found to be unaffected by temperature and dew point, therefore they are able to be used for fuels at high dew point.

Then, the results of comparison of adsorption capacities of various sulfur compounds on Ag/Na-Y at dew point -20℃ are shown in Figure 6. Ag/Na-Y was excellent in the adsorption performance of DMS and THT.

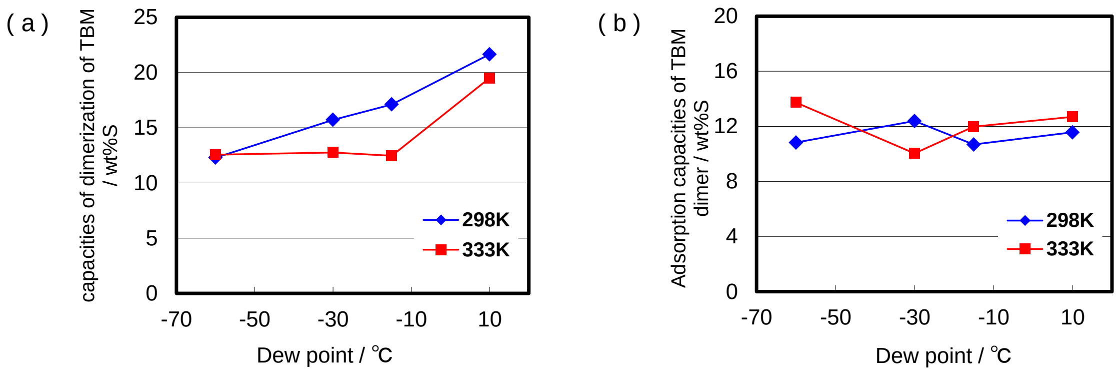

Figure 5 (a) The capacities of dimerization of TBM on agent A and (b) the adsorption capacities of TBM dimer on G2x for 8 ppm TBM and 16 ppm C_6H_{10} in desulfurized city gas with a flow rate of 1,000 cm^3 min^{-1}, SV=60,000h^{r-1}

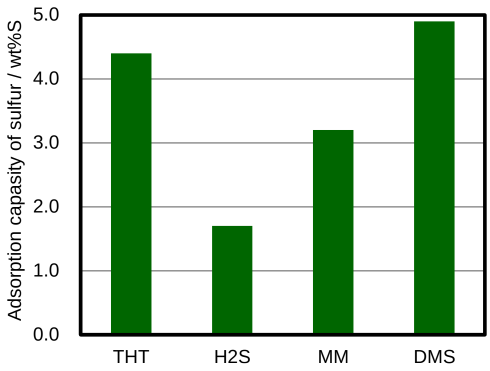

Figure 6 Comparison of adsorption capacities of impurity sulfurs on Ag/Na-Y for 10 ppm of sulfur compounds in desulfurized city gas at temperature 25℃ and dew point -20℃ (1200 ppm as water concentration), with a flow rate of 1,000 cm^3 min^{-1}, SV=60,000h^{r-1}

2.3.2. Cost estimation of the novel desulfurizer

Using the results of adsorption performance evaluation of the agents, we estimated the cost of desulfurizing agents by applying the novel desulfurizer to the city gas supplied by Tokyo Gas (Figure 7).

The novel desulfurizer consisting of the triple layers for the present odorants, TBM and C_6H_{10}, can be expected to reduce 80% of the material cost compared with the desulfurizer consisting solely of Ag/Na-Y for the previous odorants, TBM and DMS. The novel desulfurizer for the present odorants, TBM and C_6H_{10}, can be expected to reduce 60% of the material cost compared with the desulfurizer consisting solely of Ag/Na-Y for the present odorants, TBM and C_6H_{10}.

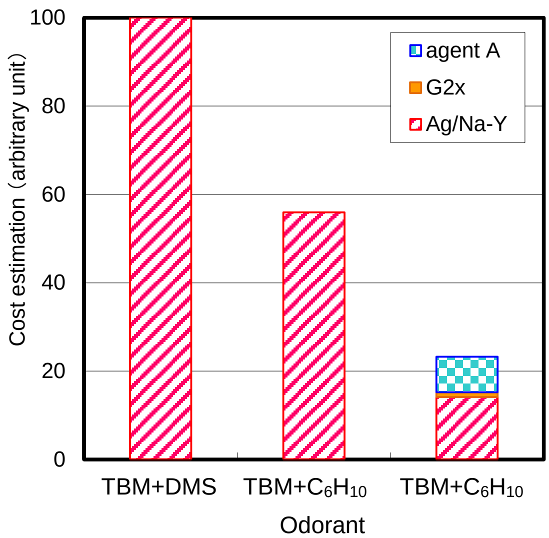

Figure 7 Comparison of the cost estimation of the novel and previous desulfurizer under the condition of the previous and present odorants

2.4. Conclusion

We developed the novel desulfurizer consisting of the triple layers utilizing dimerization reaction of TBM and succeeded in significantly reducing the volume of the expensive Ag/Na-Y by removing TBM using transition metal oxides and activated carbons. By applying the novel desulfurizer to ENE-FARM, it is expected that 80% of the material cost can be reduced.

3. References

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