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ACTIVATION OF OXYGEN FOR PARTIAL OXIDATION WITH THE FUEL CELL TYPE REACTOR USING LaGaO₃ MEMBRANE

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ABSTRACT

For the effective gasification of bio-waste, partial oxidation is very important. Sold oxide fuel cell system could be used for purification of oxygen from air. An application of fuel cell system using LaGaO₃ membrane as an electrolyte is studied. Partial oxidation of methane is studied as a model reaction. Mist decomposition method was applied to prepare anode catalyst. A mixture of (Ni+Li):Al with molar ratio of Ni:Li:Al=0.5:0.5:1 showed the highest activity. Mist decomposition method was very effective for the preparation of fine multi component electrode catalysts on the electrolyte surface. More than 80% of CO selectivity was obtained with more than 15% of conversion with more than 10% of C2 compounds.

Keywords: Partial oxidation of methane, Fuel cell reactor, Membrane reactor, LaGaIO3 electrolyte, Mist pyrolysis method

INTRODUCTION

Non-edible biomass and bio-waste are carbon neutral, renewable, and abundant resources that were proposed as one of the solutions to two of the most persistent global problems: the continuous increase in energy demand and global warming. Oxidative gasification using air attracts considerable attentions but requires additional oxygen purification process (Tagawa et al., 2013). Application of solid oxide fuel cell system as oxygen permeable membrane is one of the solutions.

In our previous studies, highly selective oxidation processes of methane were studied by using solid oxide fuel cell system as an oxygen permeable membrane reactor, The oxygen anion selective permeability through the solid oxide electrolyte membrane can remove the oxygen production plant from oxidation processes and can also give high selectivity. This system can also convert the excess energy of reaction into electricity, as is called a "Chemicals-Energy co-generation" (Tagawa et al., 1999). Non-Faradaic electrochemical modification of catalytic activity is also of recent interest for the application of (Tagawa et al., 2003). For the highly selective oxidation system, design and preparation of anode catalyst are essential (Tagawa et al., 1998 and Moe et al., 1998a),b))

A mist pyrolysis method is an effective method for preparation of fine anode particles on the surface of YSZ (Yttria Stabilized Zirconia) electrolyte (Moe et al., 1998 and Carrillo et al., 2001). As the operation temperature of YSZ (= about 1300K) is much higher than the reaction temperature of partial oxidation of methane, we have studied partial oxidation of methane with Molten Carbonate Fuel Cell (MCFC) system (Ito et al., 2001) and designed Ni based anode catalyst under milder conditions. The possibility of "Intermediate Temperature Solid Electrolyte" was also pointed out. (Tagawa et al., 2006).

In this study, Intermediate Temperature Solid Oxide Fuel Cell (=IT-SOFC) system using LaGaO₃ type electrolyte (=LSGM) was tested as a selective oxidation reactor for the partial oxidation of methane. Methane is selected as one of the model reactants from biomass gasification products. The mist pyrolysis method was tested as a preparation method of designed Ni-Li/Al2O3 anode catalyst.

EXPERIMENTAL

Solid oxide fuel cell type reactor

Figure 1 shows the schematic view of the SOFC Type Reactor. A plate type $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_3 =$ LSGM or $10Sc_2O_3$ -1CeO₂-89ZrO₂ =10Sc1CeSZ (thickness = 0.3mm, diameter = 42mm) was used as an electrolyte, which was provided by Japan Fine Ceramics Co. Ni-Li/Al₂O₃ as anode catalyst was prepared by the mist pyrolysis method on the surface of the electrolyte. The cathode catalvst $La_{0.6}Sr_{0.4}CoO_3 = LSC$ was prepared by ordinary paste method on the other side of the electrolyte. The standard operating conditions of the system was set as follows. CH₄ was fed to the anode side while air was fed to the cathode side. The flow rates of CH₄ and air were 3.72×10⁻⁶mol/s and 7.44×10⁻⁶mol/s, respectively. The reaction temperature was varied from 973K to 1223K. Reaction mixture from the anode side was analyzed by TCD-GC after removal of moisture by cold trap.

Preparation of anode catalyst

Figure 2.shows the Schematic design of mist pyrolysis method. An mixed aqueous solution of



Fig. 1 The schematic view of the Solid Oxide Fuel Cell Reactor

Ni(NO₃)₂•6H₂O, Li(NO₃), and Al(NO₃)₃•6H₂O was placed in the reservoir and atomised by ultrasonic transducer. Thusly generated mist of solution was fed under flow of air onto the electrolyte heated at 503K on the plate heater. The solution was then dried and decomposed into Ni-Li-Al anode catalyst. A periodic operation such as mist charge of 30s and following thermal treatment 30s were repeated for total 1h. Thusly prepared anode catalysts were represented as (Ni-Li):Al catalyst and molar ratio was indicated numerically like (=1:1). The sample with step-by-step method was also prepared. Alumina was deposited first by mist pyrolysis method and then Ni+Li was also deposited by mist pyrolysis method. This sample was represented as (NI-Li)/AI.

RESULTS AND DISCUSSIONS Selection of electrolyte

Among various solid oxide electrolyte, LSGM and 10Sc1CeSZ (ScCeSZ) were selected and compared. With same Ni-Li(1:1) anode and LSC cathode were applied. Figures 3-5 show the conversion, selectivity and closed circuit current, respectively. LSGM showed higher conversion at lower temperature range (Fig. 3). Current value showed similar tendency suggesting that electrochemical nature of LSGM caused this tendency (Fig. 5). As reaction temperature increased, selectivity to partial oxidation (CO) decreased and selectivity to coupling reaction (C2) increased. At higher temperatures, LSGM showed high selectivity to CO while ScCeSZ showed high selectivity to C2 (Fig.4). Because using same electrode catalysts and comparing under similar conversion, differences in selectivity could be caused by the difference of oxygen species



Fig. 2: Mist pyrolysis apparatus for anode preparation



Fig. 3 Conversion of methane at various temperatures in the SOFC reactor made of LSGM and ScCeSZ.



Fig. 4 Selectivity of methane oxidation at various temperatures in the SOFC reactor made of LSGM and ScCeSZ.

generated at the anode side. Closed circuit electromotive force showed almost identical with value of 1.0V for both samples. From these results, considering the objective for the use of partial oxidation at intermediate temperature, LSGM electrolyte was selected for the further study.

Selection of cathode materials

Among various cathode materials, $La_{0.85}Sr_{0.15}MnO_3$ (LSM) and $La_{0.6}Sr_{0.4}CoO_3$ (LSC) were compared. In the case of LSM, almost the same results as LSC which were shown in Figs. 3-5. Were observed, Therefore, latest material, LSC was used in the following study.

Selection of anode composition

In our previous studies on the catalytic partial oxidation of methane (Ito et al., 1999,a,b,c), Ni+Li/Al₂O₃ catalyst was designed. In this study, composition and preparation method of this Ni-Li-Al type anode catalyst were studied. Figure 6 shows the effect of aluminium loading on conversion of CH4. Anode catalysts were prepared by mist pyrolysis method, where amount of aluminium was changed while Ni loading was kept constant. The molar ratio of Ni and Li was also kept constant value (1:1). The reaction started as low as 950K. The conversion increased with the increase of reaction temperature. Addition of a small amount of aluminium (▲) enhanced the conversion compared to those without addition (■). Equimolar mixture of (Ni+Li):Al (●) showed the highest conversion. But excess amount of aluminium (x) reduced the activity. When Ni+Li was supported after alumina was supported ($\mathbf{\nabla}$), the enhancement effect of aluminium was not observed even with an equimolar composition of (Ni+Li):Al.

Figure 7 shows the effect of aluminium loading on selectivity. At low reaction temperature, selectivity to partial oxidation was very high. Less than 10% of complete oxidation (CO2) was observed. As the reaction temperature increased, selectivity to CO decreased while selectivity to C2 increased. Equimolar mixture of (Ni+Li):Al (•) which showed the highest conversion showed the highest selectivity to CO. More than 80% of CO selectivity was observed with more than 15% of conversion, rest of products were C2 compounds and CO2. When Ni+Li was supported after alumina was supported (\mathbf{V}), which showed no effect on conversion showed the highest selectivity to C2.

Figure 8 shows the effect of aluminium loading on closed circuit current. The similar tendency to conversion (Fig. 6) was observed on the dependence on temperature. The dependence on composition was also similar to that of conversion. The rate of oxygen permeation derived from current value agreed with the rate of oxygen consumption



Fig. 5 Closed circuit current of methane oxidation at various temperature in the SOFC reactor made of LSGM and ScCeSZ.



Fig. 6 Effects of alumina loading on conversion of methane. Ni+Li:Al anode catalysts were prepared by mist pyrolysis method with constant loading of Ni with equimolar Li where amount of alumina was varied.



Fig.7 Effects of alumina loading on selectivity of methane oxidation over Ni-Li:Al anode catalyst

derived from reaction results. Therefore the reaction was concluded to be controlled by electrochemically.

Anode preparation

Effect of preparation method of anode catalyst was examined. The mist pyrolysis method was compared with an ordinary paste method. The paste method was conducted as follows; 1) fine powders of components were mixed with glycerol, 2) the mixture was pasted onto the electrolyte plate, and 3) the plate was dried and then calcined in air.

Figure 9 shows the effect of preparation method. Conversion of methane (upper figure) and rate of methane conversion (lower figure) were compared. In both figures, mist method showed higher values especially at high temperature. However, the effect appeared to be much higher on the rate of the reaction than on the conversion.

This is because the difference in the total amount of catalyst supported between the two preparation methods. The total amount of catalyst prepared by paste method (172mg) was more than ten times larger than that of mist pyrolysis method (13.7mg). The conversion represented the overall reactivity of the cell unit. On the other hand, the rate of the reaction represented the reactivity per unit weight of the anode catalyst. These results indicated that the mist pyrolysis method gave higher overall activity in spite that the amount was smaller than paste method and that the efficient use of catalyst could be realized with mist pyrolysis method

Characterization of anode

Figs 10 and 11 shows SEM - EDX analysis of (Ni-Li):Al and (Ni-Li)/Al, respectively. These SEM figures showed that the mist pyrolysis method could provide spherical small particles as small as a few micro meters. As shown in Fig. 10, EDX analysis of (Ni-Li):Al (all components were deposited at the same time) showed that anode particles were deposited on the surface of LSM plate (La mapping) and Ni and Al located on the same particle (Ni and Al mapping). On the other hand, as shown in Fig.11, EDX analysis (Ni-Li)/AI (AI was deposited first and then Ni and Li were deposited) showed that Al2O3 (Al mapping) and Ni (Ni mapping) were located in the different particles also these particles were deposited on the LSGM surface (La mapping).

These characterization results suggest that the enhancement effect of alumina which is shown in Fig. 6 could be realized by the coexistence of Al with Ni component in the same particle.

On the other hand, the rate of the reaction shown in Fig. 9 (lower) indicated that the mist pyrolysis method gave higher overall activity in spite that the amount was smaller than paste method and that the efficient use of catalyst could be realized with mist pyrolysis method. SEM analysis showed that the



Fig.8 Effects of alumina loading on close circuit current of methane oxidation over Ni-Li:Al anode catalyst



Fig. 9 Effects of anode preparation method on methane conversion (upper) and reaction rate (lower).



Fig. 10 SEM-EDX analysis of (Ni-Li):Al=1:1 prepared by mist decomposition method. Ni,Li and Al were supported at the same time using mixed solution and then calcined at 1273K.



Fig. 11 SEM-EDX analysis of (Ni-Li)/Al=1:1 prepared by mist decomposition method. Al was deposited first and the Ni and Li was supported and then calcined at 1273K.

mist pyrolysis method could provide spherical small particles as small as a few micro meters.

CONCLUSION

An application of fuel cell system using intermediate temperature electrolyte membrane as an electrolyte is studied for partial oxidation of methane. LaGaO₃ with LSC cathode material was selected from the screening test. Mist pyrolysis method was applied to prepare anode catalyst. A mixture of (Ni+Li):Al with molar ratio of Ni:Li:Al=0.5:0.5:1 showed the highest activity. Mist decomposition method was very effective for the preparation of fine multi component electrode catalysts on the electrolyte surface. More than 80% of CO selectivity was obtained with more than 15% of conversion with more than 10% of C_2 compounds.

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