CO_2 reforming of methane over nickel catalysts supported on $La_xSr_{1-x}TiO_{3-\delta}$

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Abstract: Nickel catalysts supported on lanthanum strontium titanate have been investigated for CO_2 reforming of methane in the temperature range from 500 °C to 700 °C at which severe carbon deposition is thermodynamically expected to occur. A series of $La_xSr_{1-x}TiO_{3-\delta}$ (LST) possess mixed oxide ionic and electronic conductivity and exhibit better oxide ion conductivity at low temperatures compared with typical oxide ion conductors such as yttria-stabilized zirconia. Ball-milling and barium-doping to LST were found to accelerate removal of carbonaceous species deposited on the catalyst possibly due to enhanced redox cycle by the lattice oxygen of the support materials.

Keywords: Nickel, CO_2 reforming, Lanthanum strontium titanate.

1. Introduction

Dry reforming of methane ($CH_4 + CO_2 \rightarrow 2CO + 2H_2$) is regarded as a method of utilizing CO_2 emitted and captured in energy conversion processes. The CO/H_2 ratio of syngas produced by methane dry reforming is desirable to the following synthesis processes such as Fischer-Tropsch process and a large endothermic reaction heat $\Delta H^{\circ}_{298} = 274$ kJ mol^{-1} is favorable with respect to thermal energy recovery. In this study, dry reforming of methane is targeted to recuperate thermal energy from the exhaust heat of solid oxide fuel cells (SOFC) that need efficient heat recovery achieve excellent power generation efficiency, especially in small scale units. In Japan SOFCs of 1 kW class operated at 700 °C to 800 °C are available and those of a few hundred kW class are currently prepared for initial introduction to the market. Accordingly, this study targets the temperature range below 700 °C for methane dry reforming. Methane dry reforming at low temperatures can suffer from sever carbonaceous species deposition[1], and consequently for the removal of the deposited carbon by lattice oxygen, $La_xSr_{1-x}TiO_{3-\delta}$ (LST), which was used as SOFC anode materials[2], was employed as a support material to assist removal of carbonaceous species by the lattice oxygen[3] even at the low temperatures because of their excellent oxide ion transport property.

2. Experimental

Lanthanum strontium titanate and barium-doped lanthanum strontium titanate (LBST) were prepared by the Pechini method. Calculated amounts of citric acid and titanium isopropoxide were dissolved in ethylene glycol and stirred at 100 ºC, then desired amounts of lanthanum acetate and strontium acetate were added to the solution. For barium doping, barium carbonate was added in this stage. The mixture was heated up to 150 ºC to proceed polymerization. The resultant powder was calcined in air at 800 ºC for 4 h. Ball-milling to the powders was carried out for 24 h after this calcination step. The ball-milled LST supports are hereafter denoted as LST_bm. These powders were impregnated with an aqueous solution of nickel nitrate, followed by calcination in air at 800 ºC for 4 h. The Ni loading was fixed at 10wt%. The crystalline phases of catalysts were identified by XRD with Cu Kα. The electronic states of active metals and oxygen species were determined by XPS with Mg Kα. The specific surface area of catalysts was measured by BET method using nitrogen adsorption. Temperature programmed reduction by H_2 (H_2-TPR) and temperature programmed desorption of CO_2 (CO_2-TPD) were carried out in a flow system. The catalytic activity for CO_2 reforming of methane was evaluated in a conventional fixed-bed flow reactor at atmospheric pressure. Prior to the reaction tests, 400 mg of the catalyst was set in the reactor and then reduced in 5%H_2/Ar at 800ºC for 0.5 h. Gaseous mixture of $CH_4:CO_2 = 1:3$ was supplied to the reactor at GHSV = 10000 h^{-1}. After the reaction, temperature-programmed oxidation (TPO) was performed to quantify the deposited carbon as CO_2.

3. Results and discussion

Figure 1 shows CH_4 conversion and the amount of deposited carbon in methane CO_2 reforming over the prepared catalysts. The deposited carbon amount was calculated based on carbon balance of gaseous species at the reactor inlet and outlet. Methane conversion on the ball-milled catalyst (Ni/LST_bm) was almost identical to the pristine Ni/LST with a slight decrease at 500 ºC, whereas the deposited carbon amount was decreased and consequently the production of synthesis gas (CO + H_2) was enhanced over Ni/LST_bm. Though the barium-doped catalyst (Ni/LBST) exhibited a decrease in CH_4 conversion at 500 ºC and 600 ºC, the synthesis gas production was largely promoted, compared with Ni/LST and Ni/LST_bm. Figure 2 summarizes H_2-TPR of the catalysts. It was found by H_2-TPR that the lattice oxygen of LST_bm and LSBT was more reducible at lower temperatures than that of LST and that the amount of the reducible lattice oxygen below 800 ºC was increased on LST_bm and LSBT. In addition to this H_2-TPR result, XPS measurements revealed that the ratio of surface lattice oxygen to titanium was decreased from 3.3 to 2.7 for Ni/LST, whereas larger decrease in the ratio from 3.2 to 2.1 for Ni/LST_bm, from 2.9 to 2.0 for Ni/LBST was detected. It is considered from these results that increased amount of more reducible lattice oxygen species on Ni/LST_bm and Ni/LBST helps removal of carbonaceous species by oxidation, which leads to the increase in the synthesis gas production and the decrease in the deposited carbon amount.

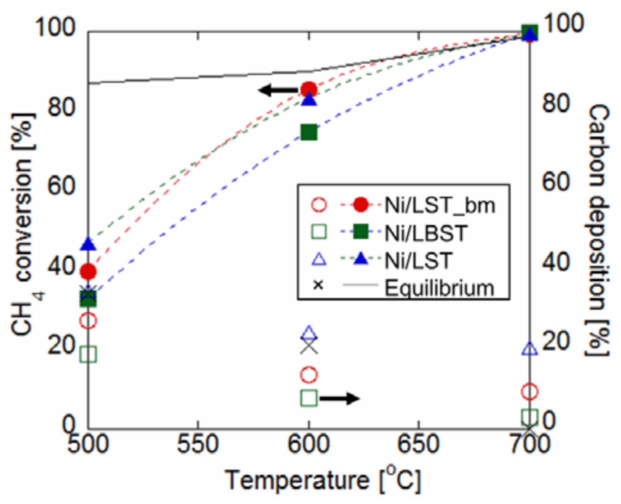

Figure 1. Methane conversion and deposited carbon amount during methane dry reforming over pristine and ball-milled Ni/$La_{0.3}Sr_{0.7}TiO_{3-\delta}$ (Ni/LST, Ni/LST_bm) and Ni/$La_{0.2}Ba_{0.1}Sr_{0.7}TiO_{3-\delta}$ (Ni/LBST).

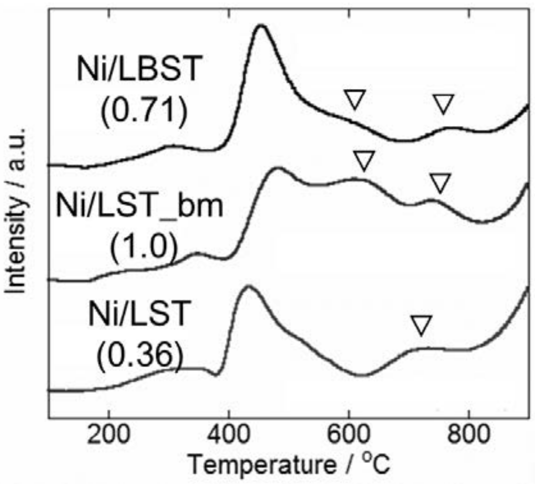

Figure 2. H_2-TPR profiles of Ni/LST, Ni/LST_bm, and Ni/LBST. The open inverted triangles designate the reduction of the lattice oxygen. The values in the blanket represent the amount of the lattice oxygen reducible below 800 °C (mmol g-cat^{-1}).

4. Conclusions

Nickel catalysts supported on lanthanum strontium titanate (LST) based oxide were investigated for CO_2 reforming of methane. Ball-milling and barium-doping to LST were effective in promoting syngas production and suppression of carbon deposition. The ball-milling and barium-doping to LST promoted the reducibility of the lattice oxygen of the supports with an increase in the amount of the reducible lattice oxygen, leading to the enhanced syngas production and carbonaceous species removal in low temperature dry reforming of methane.

References

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