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Original Research Paper

Preparation of metal catalyst component doped perovskite catalyst particle for steam reforming process by chemical solution deposition with partial reduction

Tomoya Ohno [a,*], Shohno Ochibe [a], Hideki Wachi [a], Shigeto Hirai [a], Takashi Arai [b], Hisao Suzuki [c], Takeshi Matsuda [a]

[a] Faculty of Engineering, Kitami Institute of Technology, 165 Kouen-cho, Kitami, Hokkaido 090-8507, Japan
[b] National Institute of Technology, Numadu College, 3600 Ohoka, Numadu, Shizuoka 410-8501, Japan
[c] Graduate School of Science and Technology, Shizuoka University, 3-5-1 Johoku, Hamamatsu, Shizuoka 432-8561, Japan

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ABSTRACT

Co-doped $LaAlO_3$ nanoparticles with partial reduction were applied as a catalyst to ethanol steam reforming. Co-doped $LaAlO_3$ nanoparticles were prepared using chemical solution deposition. The Co component was generated on the nanoparticle surface by a partial reduction process. The estimated H_2 yield of the ethanol steam reforming process was changed by altering the reduction conditions, although the surface areas of the reduced nanoparticles were almost equal. The highest H_2 yield was attained at 943 K reduction temperature. The calculated H_2 yield and the conversion ratio were, respectively, 78% and 99%. Reaction bi-products during steam reforming were measured to elucidate the change of the H_2 yield with the reduction temperature.

1. Introduction

Steam reforming is an important process to produce hydrogen for fuel cell units. In general, methane steam reforming is used commercially for hydrogen generation. In contrast, steam reforming using other hydrocarbons such as alcohol [1–3], toluene [4,5], and glycerol [6] present difficulties related to the catalyst. For example, Ni loaded Al_2O_3 (Ni/Al_2O_3) catalyst is the major catalyst for methane steam reforming process. However, if Ni/Al_2O_3 catalyst is applied to ethanol steam reforming, then carbonaceous materials deposit on the Ni/Al_2O_3 catalyst surface [7], thereby decreasing the catalytic activity. To suppress this phenomenon, perovskite materials have received much attention for use as a catalyst for steam reforming because perovskite catalysts exhibit stable activity with high resistance to coking in partial oxidation of hydrocarbon [8–10]. Therefore, many researchers have reported perovskite catalyst effects on catalytic activity during steam reforming. Some reports of the relevant literature describe investigations of perovskite catalysts with small surface area and low dispersibility of the metal catalyst, such as Ni and Co, on the perovskite because the perovskite material surface is flat [11].

In our earlier research, Ni-doped $LaAlO_3$ (LAO) catalyst with partial reduction process was applied to mitigate low dispersibility of the metal catalyst component on the perovskite [10]. Results show that Ni-doped LAO catalyst has high H_2 yield compared with that of the Ni-loaded LAO catalyst produced using a conventional impregnation process. We confirmed sintering of the generated Ni component during steam reforming because we were unable to control the amount of Ni component by H_2 reduction (partial reduction process). The surface area and the inside of the particles were reduced by partial reduction processes, resulting in a large amount of the generated Ni component sintered during the steam reforming process. Here, Co in the perovskite structure ($LaCoO_3$) is known as the only slightly reducible metal compared with Ni in the perovskite structure ($LaNiO_3$) [12]. Therefore, we expected that the surface area of the Co component (small amount of Co component) reduced by the partial reduction process, resulting in a highly dispersed Co component on the perovskite catalyst. Based on the assumption described above, Co-doped LAO catalyst was applied in this study as the catalyst for ethanol steam reforming. Furthermore, effects of the reduction conditions on the catalytic activity of the Co-doped LAO catalyst with the partial reduction process were investigated.

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* Corresponding author.
E-mail address: ohno@mail.kitami-it.ac.jp (T. Ohno).

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2. Experimental procedure

2.1. Particle preparation

Co-doped LAO nanoparticles with $La(Al_{0.5}Co_{0.5})O_3$ composition were prepared by chemical solution deposition. Lanthanum nitrate hexahydrate, aluminum iso-propoxide, and cobalt acetate tetrahydrate were selected as the starting reagents. First, lanthanum nitrate hexahydrate and cobalt acetate tetrahydrate were dried at 423 K for 1 h to remove the hydrate. Subsequently, lanthanum nitrate was dissolved into 2 methoxymethane at room temperature. Nitric acid was added to the lanthanum precursor solution with $[HNO_3]/[La] = 1.5$ to adjust pH of the precursor solution. Aluminum iso-propoxide and cobalt acetate were dissolved separately into 2-methoxyethanol at 423 K for 2 h. Subsequently, aluminum and cobalt precursor solutions were mixed at 273 K for 2 h. Finally, a lanthanum precursor solution and aluminum–cobalt precursor solution were mixed at 273 K for 2 h to obtain $La(Al_{0.5}Co_{0.5})O_3$ precursor solution. The precursor particle was obtained using conventional evaporation using the prepared precursor solution. Pre-annealing and annealing were conducted, respectively, at 673 and 1073 K for 3 h.

Furthermore, $LaCoO_3$ (LCO) and LAO were prepared using chemical solution deposition to estimate the thermal decomposition of the easily reducible part and the nondeductible part. The starting reagents and the experimental procedures were almost identical: LCO precursor solution was prepared by mixing of the La and Co precursor solutions. By contrast, LAO precursor solution was prepared by mixing of La and Al precursor solutions. The pre-annealing and annealing were also conducted under the same conditions.

2.2. Particle characterization

The crystal size and the phase were estimated using X-ray diffraction (XRD, D8 Advance; Bruker AXS GmbH) with copper Kα radiation. XRD patterns were collected using the step scan mode with 0.02° of step width and 5 s of step time. In addition, the (2 0 0) plane of the obtained sample was estimated with 0.01° of step width and 10 s of step time to compare the respective peak positions of Co-doped LAO and undoped LAO. The obtained XRD patterns were fitted by a Voigt function to clarify the full width at half maximum and the peak position. Elemental mapping of the prepared nanoparticles was investigated using a transmission electron microscope (TEM, JEM-2100F; JEOL) with energy dispersive X-ray spectrometry (EDS).

The surface area of the reduced sample was estimated using the adsorption isotherm of N_2 using the BET equation. After the reduction process, the adsorption isotherm N_2 was measured at 77 K using a conventional high-vacuum static system.

2.3. Catalytic activity

The obtained $La(Al_{0.5}Co_{0.5})O_3$ nanoparticles were reduced at several conditions at 823–998 K for 1 h under H_2 flow (30 mL/min) to generate metal Co on the surface. The catalytic activity of the ethanol steam reforming process was estimated at 823 K under atmospheric pressure in a conventional fixed bed reactor. A mixture of steam, ethanol and nitrogen with a molar ratio (H_2O/C_2H_5OH) of 5 was introduced onto the catalyst bed at the W/F of 2.0 g-cat·h/C_2H_5OH mol. Here, nitrogen was used as an internal standard. The outlet gas was estimated using a gas chromatograph (GC, GC-14B; Shimadzu Corp.) with a thermal conductivity detector (TCD) and a flame ionization detector (FID). The concentrations of H_2, CO, CO_2, and CH_4 in the outlet gas were determined by TCD using an activated charcoal column for separation. Ethanol, acetaldehyde and hydrocarbons were analyzed with FID using TC-1 and Unipak S separation columns. The H_2 yield was calculated using Eq. (1).

$$\gamma_{H2} = \frac{F_{H2}^{out}}{6 \times F_{C2H5OH}^{in}} \times 100\ (\%) \tag{1}$$

In that equation, γ_{H2}, F_{H2}^{out} and F_{C2H5OH}^{in} denote the hydrogen yield, the flow rate of H_2 gas in the outlet gas, and the flow rate of ethanol in the inlet gas. The catalytic activity test was conducted under the same conditions as those described in our past reports [10] to ascertain the effects of the kind of metal catalyst on the catalytic activity.

3. Results

3.1. Crystal structure

The crystal structure of the prepared $La(Al_{0.5}Co_{0.5})O_3$ nanoparticles is depicted in Fig. 1. The inset presents a comparison of the (2 0 0) reflection of the prepared Co-doped LAO and the undoped LAO. The measured XRD pattern portrays the prepared Co-doped LAO as perovskite mono-phase. The (2 0 0) peak position shifted to a lower angle compared with that of the undoped LAO. The lattice constant of the LAO and LCO has been reported, respectively, as 3.791 [13] and 3.820 [14] Å. Therefore, the estimated peak shift to be lower angle by Co doping is the reasonable result. In addition, the estimated lattice constants of prepared LAO and Co-doped LAO were, respectively, 3.794 and 3.806 Å. From the result presented above, we concluded that the Co element was doped into the B-site of the LAO perovskite lattice.

Co-doped LAO comprises the nonreducible metal oxide (LAO) part and the easily reducible metal oxide (LCO) part. The LCO part is partially reduced under the reduction process to generate the metal catalyst (Co) component on the metal oxide particles. Therefore, the effect of the reduction temperature on the LCO decomposition was estimated using XRD analysis. Fig. 2 portrays the change in the crystal phase of the reduced $LaCoO_3$ with different reduction temperatures. From Fig. 2, LCO with perovskite phase was completely reduced to La_2O_3 and Co at 773 K reduction temperature although the thermal decomposition started from 673 K reduction temperature. However, LAO has no thermal decomposition at 973 K reduction temperature. Based on these results, we inferred that

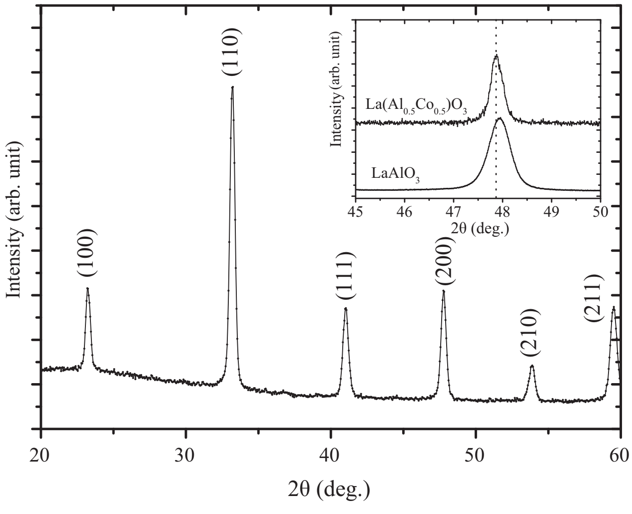

Fig. 1. XRD pattern of the obtained $La(Al_{0.5},Co_{0.5})O_3$ nanoparticles.

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