Advanced Powder Technology 27 (2016) 179–183

Contents lists available at ScienceDirect

Advanced Powder Technology

journal homepage: www.elsevier.com/locate/apt

Original Research Paper

Effect of the reduction condition on the catalytic activity for steam reforming process using Ni doped $LaAlO_3$ nano-particles

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ARTICLE INFO

Article history:
Received 25 August 2015
Received in revised form 20 November 2015
Accepted 30 November 2015
Available online 14 December 2015

Keywords:
Nanoparticles
Chemical solution deposition
Steam reforming process
Catalyst

ABSTRACT

Ni doped lanthanum aluminate (LAO) was prepared by chemical solution deposition, and the Ni component was generated on the surface of Ni doped LAO by the H_2 reduction process. The obtained Ni doped LAO was perovskite mono-phase. The specific surface area and the reduction degree of the obtained catalyst was controlled by control the reduction conditions. As a result, almost the all Ni component near the surface was reduced by H_2 reduction process even in the case of low H_2 reduction temperature, although the catalytic activity changed depends on the reduction temperature. Thus, we concluded that the reduced perovskite part was also important factor to determine the catalytic activity in the case of Ni doped LAO catalyst. The highest catalytic activity (H_2 yield) was attained under the 873 K reduction temperature.

1. Introduction

Recently, perovskite materials had been reported as a novel catalyst materials for steam reforming process [1–4], because these materials exhibit stable catalytic activity with high resistance to coking in partial oxidation of methane. However, several reports indicated that the perovskite catalyst have still some subjects such as a small specific surface area and a low dispersibility of metal catalyst component on the surface, resulting in the low catalytic activity [5].

In our previous studies, the BTO hollow particles with relatively large specific surface area was prepared by chemical solution deposition and the metal catalyst of Ni was loaded onto the BTO hollow particles by the conventional impregnant method [6]. The obtained Ni/BTO hollow particles was applied to the methane and ethanol steam reforming process, and the relatively high H_2 yield was observed. However, the low dispersibility of metal catalyst (Ni) on the BTO suppressed the catalytic activity.

In general, metal component such as Ni and Co was impregnated on the surface of perovskite materials to apply as the catalyst for steam reforming process [7,8]. However, there are no meso-pore on the surface of almost the all perovskite materials. Therefore, the size of the metal component on the perovskite increased compared with that on the surface of zeolite such as ZSM-5 [9]. Recently, our research group applied new strategy to solve this subject. Then, the metal component such as Ni was doped into the perovskite lattice, subsequently the metal component was generated on the surface of perovskite by the reduction process. In the case of this method, the reduction process is the most important factors to design the surface morphology of the catalyst. Therefore, we estimated the effect of the reduction condition on the catalytic activity and the surface morphology of the Ni doped $LaAlO_3$ (LAO) catalyst in this study.

2. Experimental procedure

2.1. Preparation of the catalyst

Ni doped LAO catalyst was prepared by chemical solution deposition (CSD). Lanthanum nitrate hexa-hydrate, nickel acetate tetra-hydrate and aluminum isopropoxide was selected as starting reagents of the precursor solution. In this study, the amount of nickel content was fixed to be $La(Al_{0.5}Ni_{0.5})O_3$ composition. Firstly, Lanthanum nitrate hexa-hydrate and nickel acetate tetra-hydrate was dried at 423 K for 1 h to remove the hydrate. Subsequently, lanthanum nitrate, nickel acetate and aluminum isopropoxide was separately dissolved into 2-methoxyethanol at room temperature.

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http://dx.doi.org/10.1016/j.apt.2015.11.013
0921-8831/

In our previous study, under the ice bath condition during mixing of lanthanum and alumina precursor solutions was one of the key factors to prepare the pure LAO precursor solution [10]. Therefore, lanthanum and aluminum precursor solutions was mixed at 273 K for 2 h, after that the obtained lanthanum aluminate precursor solution and nickel precursor solution was mixed at 273 K for 1 h to obtain Ni doped LAO precursor solution. The precursor particle was obtained by conventional evaporating process. The pre-annealing and annealing was carried out at 673 and 1073 K for 3 h, respectively.

2.2. Estimation of the reduction degree

The obtained Ni doped LAO was reduced at several conditions in the range from 823 to 1073 K for 1 h under H_2 flow (30 mL/min). The reduction degree was estimated by the vacuum system. The approximately 0.1 g sample was loaded into the tube reactor, and the samples were reduced by several reduction conditions with different temperature. The dead volume of the reactor was measured by He gas. After that, the reduced samples were oxidized by the stocked O_2 at 873 K. Subsequently, the used O_2 by the oxidation of the sample was measured by pressure sensor. Lastly, the reduction degree was calculated from the amount of the used O_2.

2.3. Characterization of the catalyst

The microstructure of the obtained catalyst was observed by transmission electron microscope (TEM, JEM-2100F, JEOL). The obtained catalyst was kept into the resin, and the sample was treated by Ion Slicer (EM-09100, JEOL) to observe the cross sectional TEM image of the nanoparticles.

The crystal structure and the size was measured by X-ray diffraction (XRD, D8 Advance, Bruker AXS GmbH) with the 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 sample was measured by 0.01° of step width and 10 s. of step time to compare the peak positions between the Ni doped LAO and undoped LAO. The obtained XRD patterns were fitted by Voigt function to estimate the full width at half maximum and the peak position.

The specific surface area of the reduced sample was estimated by 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.

2.4. Catalytic activity

Steam reforming of ethanol was carried out at 873 K under atmospheric pressure in a conventional fixed bed reactor. A mixture of ethanol, steam and N_2 with a molar H_2O/C_2H_5OH ratio of 5 was introduced onto the catalyst bed at the W/F of 2.0 g-cat h/C_2H_5OH-mol. Here, N_2 was used as an internal standard. The outlet gas was estimated by gas chromatograph (GC, GC-14B, Shimadzu Co.) with thermal conductivity detector (TCD) and flame ionization detector (FID). The concentration 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 by Eq. (1).

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

Here, γ_{H2}, F_{H2}^{out} and F_{C2H5OH}^{in} indicate the hydrogen yield, the flow rate of H_2 gas in the outlet gas and the flow rate of ethanol in the inlet gas

3. Results

3.1. Crystal structure

Fig. 1 shows the XRD pattern for the obtained Ni doped LAO particles. The inset shows the comparison of the (2 0 0) reflections of the obtained Ni doped LAO and undoped LAO. From Fig. 1, the obtained Ni doped LAO was perovskite mono-phase. In addition, the peak position of the (2 0 0) reflection shifted to lower angle compared with that of the undoped LAO which possibly due to the increase of the lattice constant by Ni doping. Here, the lattice constant of the LAO and $LaNiO_3$ has been reported as 3.79 and 3.86 Å, respectively [11,12]. The calculated lattice constant of the obtained 50% Ni doped LAO was 3.82 Å. Therefore, we considered the Ni was successfully doped to LAO lattice by this preparation method.

Slagtern et al. reported the $LaNiO_3$ lattice was easily destroyed by H_2 reduction process [13]. In this study, H_2 reduction process was required to generate Ni catalyst component on the surface. However, the perovskite structure was also required for catalyst of steam reforming. Therefore, we estimated the appropriate reduction condition by change the reduction condition. Fig. 2 shows the XRD pattern for the Ni doped LAO after the reduction process with different reduction temperature. From Fig. 2, the perovskite structure was still remained up to 923 K reduction temperature. In addition, the faint amount of Ni was detected at around $2\theta = 45$ degree. In the case of undoped LAO, the perovskite structure was not destroyed by H_2 reduction process [10]. Therefore, we concluded that La–O–Al bond lead to the stability of Ni doped LAO under the H_2 reduction process. From the XRD analysis, we considered the surface part of the Ni doped LAO was reduced by H_2 reduction process, although the core part was still perovskite structure.

3.2. Surface morphology

Fig. 3 portrays the typical TEM images of the obtained Ni doped LAO particles before and after reduction process at 873 K for 1 h. The inset shows the Fast Fourier Transform image of the selected area (the black square area in the image). After the H_2 reduction process, approximately 2 nm depth from the surface of the obtained particles has no lattice line (Fig. 3(a)), although the lattice line was completely identified in the case of the before H_2 reduction process (Fig. 3(b)). Form Figs. 2 and 3, we confirmed that just

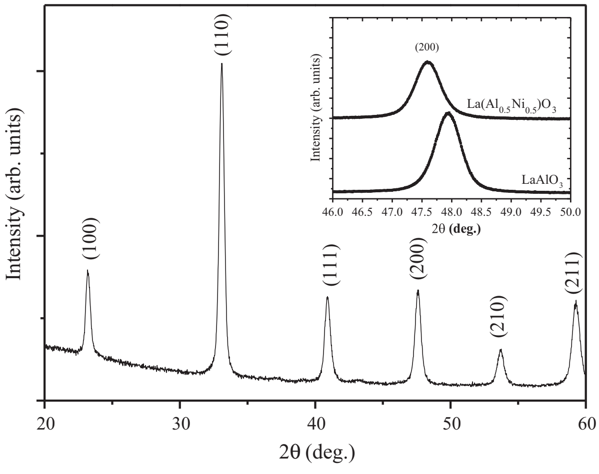

Fig. 1. XRD pattern of the obtained $La(Al_{0.5}Ni_{0.5})O_3$ catalyst.