Structural and catalytic properties of $LaNiO_3$ and $NiO/LaNiO_3$ for CO oxidation prepared by hydrolysis method

Takuya Kawamoto, Ryo Ichitsubo, Hajime Hojo, Hisahiro Einaga*

Department of Advanced Materials Science and Engineering, Faculty of Engineering Sciences, Kyushu University, Kasuga, Fukuoka, 816-8580 Japan

**Corresponding author: Fax number+81-92-583-8853, E-mail address einaga.hisahiro.399@m.kyushu-u.ac.jp*

Abstract: We prepared $LaNiO_3$ perovskite oxides by hydrolysis method using tetramethylammonium hydroxide. $LaNiO_3$ perovskite phases were formed and the formation behavior of impurity NiO phase was controlled by changing calcination temperature. The deposition of NiO particles on the $LaNiO_3$ surface improved the CO oxidation activity of $LaNiO_3$ catalyst due to the interaction between NiO and $LaNiO_3$ phases. The NiO loaded $LaNiO_3$ catalyst exhibited higher activity for CO oxidation than supported Pt catalyst. The mechanism for CO oxidation was investigated based on TPR, HAADF-STEM, and Ni K-edge XAFS studies.

Keywords: $LaNiO_3$, perovskite oxides, CO oxidation.

1. Introduction

Air pollution is getting worse on a global scale in recent years, and air purification catalysts with high oxidation activity are highly required. Carbon monoxide (CO), hydrocarbons (HC), nitrogen oxides (NOx), and volatile organic compounds (VOC) are the harmful to be removed from exhaust gases. To remove these air pollutants, catalytic oxidation process with inexpensive catalysts without the use of platinum (Pt) and palladium (Pd) should be developed.

As the inexpensive catalysts to replace noble metal catalysts, perovskite type oxides (ABO3) have been extensively used. Due to high structural stability and oxidation activity, perovskite type oxides can be used as a purification catalyst for complete oxidation of HC, CO, NOx and VOCs. We found that $LaNiO_3$ showed high oxidation activity for CO, and the addition of Ce improves the activity. The Ce-added LaNiO3 was mainly composed of $LaNiO_3$ perovskite oxides structure with small particles of CeO_2 and NiO. The catalyst showed highly activity than $LaNiO_3$ with single phase, indicating that the metal oxide / perovskite mixed oxide composites are good oxidation catalysts. In this study, we investigated the effect of catalyst composition on the activity of La-Ce-Ni catalyst to clarify the factors controlling catalytic activities.

2. Experimental

The La-Ce-Ni catalysts were prepared using the Reverse Homogeneous Precipitation (RHP) method. Metal nitrates were mixed in a stoichiometric ratio and dropped to tetramethyl ammonium hydroxide (a precipitating agent) to obtain precursor hydroxides, which were dried at 100°C overnight and calcined at 850°C for 5 h.

To identify the crystal phase of prepared catalysts, X-ray diffraction (XRD) measurement was performed. Temperature programmed reduction of the catalyst with hydrogen (H_2-TPR) was carried out to study the reactivity of the catalyst surface and lattice oxygen. The sample (0.05g) was pretreated in air at 550 ºC for 1 h and then cooled to 50 ºC. Subsequently, the gas flow was switched to H_2 and the temperature was raised from 50 ºC to 850 ºC with a heating rate of 10 ºC/min to record the hydrogen consumption profile. The CO oxidation activity test was carried out with a fixed bed flow type reaction apparatus with a flow rate of 500 mL / min (CO-0.5%/O_2-0.25%/N_2-balance) and catalyst amount of 0.1 g at a reaction temperature of 200 °C.

3. Results and discussion

XRD and Ni-K edge EXAFS studies showed that $LaNiO_3$ perovskite phases were formed for the samples prepared by hydrolysis method with TMAH and calcined at 650-950ºC. These studies revealed that impurity NiO phases were also present for the samples. The formation behavior of NiO phase depended on the calcination temperature: the peak due to Ni-O bond decreased in its intensity with increasing the calcination temperature and the formation of Ni-O was suppressed by calcination at 850°C.

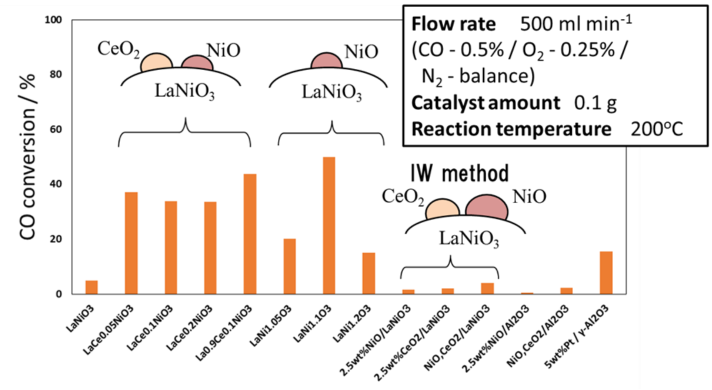

Figure 1. Catalytic oxidation of CO over $LaNiO_3$-based mixed oxides.

The $LaNiO_3$ catalyst exhibited higher activity for CO oxidation than $LaCoO_3$ which are commonly used as CO oxidation catalysts in the temperature range of 150-500°C. H_2-TPR profile showed two reduction peaks in the lower temperature range (250-430ºC) due to the reduction of Ni^{3+} to Ni^{2+} concomitant with structural change from $LaNiO_3$ to La_2NiO_4 and higher temperature range (450-600°C) due to the reduction of Ni^{2+} and Ni^0 deposition. The reduction temperatures were lower for $LaNiO_3$ than $LaCoO_3$, indicating that the $LaNiO_3$ catalyst was more easily reducible. In addition, CO-TPR profiles showed that CO consumption (CO_2 formation) temperatures were lower for $LaNiO_3$ than $LaCoO_3$ and implying that the reactivity of surface lattice oxygen species with CO is higher for $LaNiO_3$ catalyst. The reactivity of these oxygen species was reflected in the catalytic properties of $LaNiO_3$ than $LaCoO_3$.

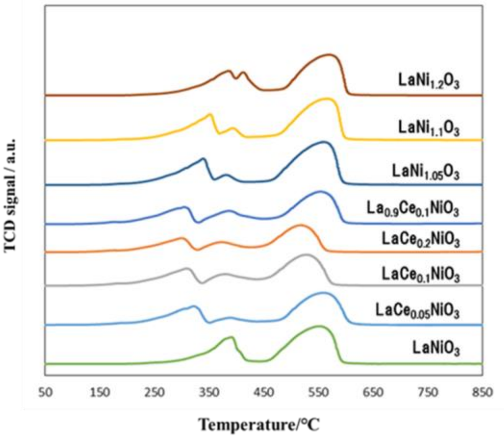

Figure 2. H_2-TPR profiles for $LaNiO_3$-based mixed oxides.

When the catalyst was prepared by the same methods with Ni/La ratio of 1/1, the impurity phase NiO was formed, which was confirmed by XRD patterns and Ni K-edge EXAFS spectra. The catalyst (denoted as $NiO/LaNiO_3$) exhibited much higher activity than $LaNiO_3$ catalyst and even than 5wt%-Pt/γ-Al_2O_3 catalyst in the temperature range of 100-200ºC (Figure 1). The $LaNiO_3$ catalysts exhibited steady state activity for CO oxidation. HAADF-STEM observation showed that NiO particles with the size of 40 nm were deposited on the surface of $LaNiO_3$. This finding suggests that NiO on $LaNiO_3$ perovskite phase also improve catalytic properties.

The deposition of NiO particles on the $LaNiO_3$ further reduced the temperature for H_2 reduction. H_2-TPR profiles and in situ Ni K-edge XAFS studies showed that H_2 consumption temperature decreased by the deposition of NiO particles. The NiO particles on $LaNiO_3$ were not reduced by H_2 and CO in the reaction temperature range (100-200ºC), suggesting that the interaction between NiO and $LaNiO_3$ phases facilitates the reaction of surface lattice oxygen with CO.

4. Conclusions

In this study, we investigated the structural and catalytic properties of $LaNiO_3$ and $NiO/LaNiO_3$ catalysts prepared by hydrolysis method. The catalysts showed higher activity for CO oxidation than other perovskite oxides and the deposition of NiO particles on the $LaNiO_3$ greatly improved the CO oxidation activity due to the promoted reactivity of surface oxygen. These findings suggested that control of the interaction between metal oxide/perovskite mixed oxides interface is a promising method for improving the reactivity.

References

1. J. Hwang, R. R. Rao, L. Giordano, Y. Yu, Y. Shao, Science 358 (2017) 751.
2. S. Royer, D. Duprez, F. Can, X. Courtois, C. Batiot-Dupeyat, S. Laassiri, H. Alamdari, Chem. Rev. 114 (2014) 10292.