Low Temperature-Water Gas Shift Reaction Using Perovskite-type Oxide Catalyst Containing Cerium Ion

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Significance and Relevance

The perovskite-type oxides containing Ce ion were successfully prepared by the thermal decomposition of heteronuclear metal cyano complexes. The present of trivalent Ce ion at A-site of perovskite-type oxide (ABO_3) was confirmed by several techniques. Ni/$La_{0.7}Ce_{0.3}FeO_3$ catalyst showed higher catalytic activity for the reverse water gas shift reaction ($CO_2 + H_2 \rightleftarrows CO + H_2O$) at low temperature than Ni/CeO_2 catalyst.

Introduction and Motivations

It is well known that perovskite-type oxide catalysts (ABO_3) are highly active in complete oxidation reactions such as CO and PM oxidation. It has been reported that the catalytic activity can be greatly enhanced by substituting a part of the A-site metal ions with other metal ions. For example, partial substitution of Sr ions in $LaMnO_3$ improved the activity of propane oxidation[1]. In some cases, a valence change of metal ions occurs during the catalytic reaction; the Pd^{2+} ions are reported to exist at the lattice points of perovskite-type oxides in an oxidizing atmosphere and exit to the surface as metal in a reducing atmosphere. In this study, we focus on Ce ions, which have redox properties of +3/+4 depending on the oxygen partial pressure. This study reports a new preparation of $LaFeO_3$ catalysts with partial substitution of Ce ions and the reverse water gas shift reaction (RWGS reaction) using this catalyst.

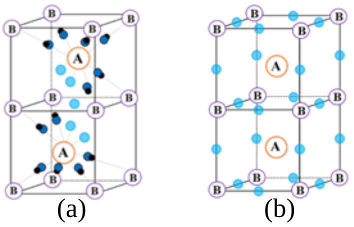

Figure 1. Structures of (a) heteronuclear metal cyano complex and (b) perovskite-type oxide

Materials and Methods

We have reported that ABO_3 catalyst can be prepared by thermal decomposition of heteronuclear cyano metal complex precursor (CN method)[2, 3]. This new method is expected to yield ABO_3 catalyst with high surface area and high homogeneity due to the similarity of precursor and product structures (Fig. 1). The heteronuclear metal cyano complexes, $AA'[B(CN)_6]\cdot nH_2O$ (A = lanthanide metal ion, A' = cerium ion, B = iron or cobalt ion), were prepared and calcined at 500-1000 °C to yield $A_{1-x}A'_xBO_3$ catalyst. The resulting catalysts were characterized by XRD, BET, H_2-TPR, XAFS (XAS), EIS, and ASR methods. The RWGS reaction was performed under the following reaction condition: CO_2 conc. = 2.5%, H_2 conc. = 10%, He balance, total flow rate = 100 cm^3min^{-1}, catalyst weight = 0.2 g). The product gas was analyzed by gas chromatography (TCD).

Results and Discussion

Figure 2 shows XRD patterns of $La_{1-x}Ce_x[Fe(CN)_6]\cdot nH_2O$ calcined at 700 °C for 1 h. Two sets of peaks assigned to perovskite-type structure ($0 \le x \le 0.3$) and fluorite-type structure ($0.15 \le x \le 0.30$) were observed. All XRD peaks due to the perovskite-type structure shifted to higher angles with increasing x. This means that the lattice constant of the perovskite-type oxide decreases with increasing x, suggesting that Ce ions are incorporated into the lattice of the perovskite-type oxide. Hereafter, $La_{1-x}Ce_x[Fe(CN)_6]\cdot nH_2O$ calcined at 700°C is denoted as $La_{1-x}Ce_xFeO_3$(700), but the sample with more Ce ions contains CeO_2 other than perovskite-type oxides.

H_2-TPR measurements were conducted for $La_{1-x}Ce_x[Fe(CN)_6]\cdot nH_2O$ calcined at 700 °C for 1 h. The results are shown in Fig. 3. No reduction peak was observed for the sample with x = 0 ($LaFeO_3$) up to 900 °C. The reduction peaks of samples with $0.05 \le x \le 0.30$ were observed in the temperature range of 200-500 °C. The intensity in reduction peak increased with increasing x, indicating that the reduction of sample was accelerated by Ce ion. The reduction peak of $La_{1-x}Ce_x[Fe(CN)_6]\cdot nH_2O$ ($0.05 \le x \le 0.30$) calcined at 700 °C was very similar to that $La_{1-x}Sr_xFeO_{3-\delta}$[4], suggesting that perovskite-type oxide partially substituted by Ce ion possesses the oxidation ability like that partially substituted by Sr ion. The result of X-ray absorption spectroscopy suggests that Ce ion exists as trivalent ion in bulk of perovskite-type oxide.

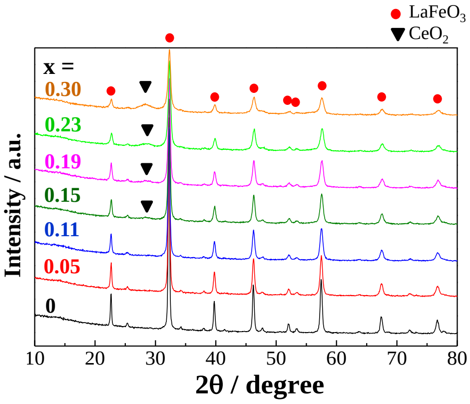

Figure 2. XRD patterns of $La_{1-x}Ce_x[Fe(CN)_6]\cdot nH_2O$ calcined at 700 °C for 1 h

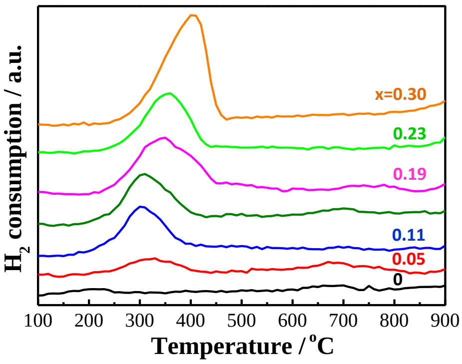

Figure 3. XRD patterns of $La_{1-x}Ce_x[Fe(CN)_6]\cdot nH_2O$ calcined at 700 °C for 1 h

Figure 4 shows the catalytic activity of $La_{1-x}Ce_xFeO_3$(700) for RWGS reaction. The Ni/CeO_2, catalyst[5] showed low activity below 400 °C. On the other hand, $LaFeO_3$ showed relatively high catalytic activity, and the catalytic activity was slightly enhanced by Ni addition. $La_{0.7}Ce_{0.3}FeO_3$(700) catalyst is not so active for RWGS reaction; however, its catalytic activity was extremely improved by the addition of Ni. It was found that the activity of Ni/$La_{0.7}Ce_{0.3}FeO_3$(700) catalyst was 10 times larger than that of Ni/CeO_2 catalyst (390 °C).

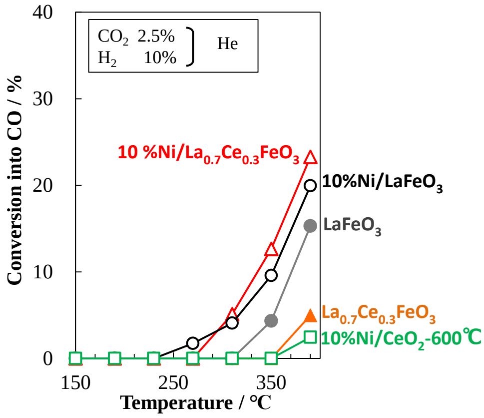

Figure 4. Catalytic activities for RWGS reaction over $La_{1-x}Ce_xFeO_3$(700) with and without Ni loading

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