NOTE

TREATMENT OF EXHAUST GASES FROM A METHANOL FUELED VEHICLE OVER PEROVSKITE OXIDE CATALYSTS

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Abstract—As a study on the treatment of exhaust gases from a methanol-fueled vehicle, catalytic oxidation of formaldehyde and methanol on perovskite-type oxides was performed. $La_{0.8}Sr_{0.2}MnO_3$, $La_{0.8}Sr_{0.2}CoO_3$, $YBa_2Cu_3O_7$ (superconductor), and $ErBa_2Cu_3O_7$ (superconductor) were used as catalysts. La-based catalysts were prepared by a citrate method and calcined at 650℃, 800℃, and 900℃, respectively. The catalytic activity of La-based catalysts increased with the increase in the surface area that was dependent on the calcination temperature. Superconductive oxides were also prepared by a citrate method and calcined at 920℃. The catalytic activity of $ErBa_2Cu_3O_7$ was found to be better than that of $YBa_2Cu_3O_7$. For La-based perovskite calcined at 650℃, the catalytic activity of $La_{0.8}Sr_{0.2}MnO_3$ was higher than $La_{0.8}Sr_{0.2}CoO_3$. Calcining at 800℃ and 900℃, however, the catalytic activity of $La_{0.8}Sr_{0.2}CoO_3$ was higher than $La_{0.8}Sr_{0.2}MnO_3$.

INTRODUCTION

Exhaust gases of a methanol-fueled vehicle are different in the composition of hydrocarbon constituents from those of a gasoline-fueled vehicle. The pollutant gas from a gasoline-vehicle contains a wide range of hydrocarbons, carbon monoxide, and nitrogen oxides, whereas the exhaust from a methanol-vehicle consists mainly of unburned methanol (0.1 mole%), formaldehyde (0.1 mole%), carbon monoxide (0.5 mole%), a trace amount of oxygenated hydrocarbon species and negligible amount of SO_x and NO_x [1].

Noble metals such as Pt, Pd, and Rh were proved to be useful for the treatment of the exhaust gas from methanol vehicle [2-4], but base metal catalysts are also expected to be useful for the same purpose, because methanol has much lower sulfur content than gasoline.

In this study, catalytic oxidation of HCHO and CH_3-OH, which were major components in the exhaust gas from the methanol-fueled vehicle, was performed on $La_{0.8}Sr_{0.2}BO_3$ (B=Mn, Co), $ErBa_2Cu_3O_{7-x}$ and $YBa_2Cu_3O_{7-x}$.

EXPERIMENTAL

La-based perovskites and oxide-superconductors

were prepared by the citrate method [5]. A stoichiometric amount of nitrate of each component (La:Sr:Co or Mn=0.8:0.2:1) was dissolved in distilled water and then mixed thoroughly with the corresponding stoichiometric amount of citric acid solution. This solution was evaporated at 70℃ in a vacuum dryer to form a gel state and then it was calcined at 650℃, 800℃, and 900℃, respectively. Oxide-superconductors were calcined at 920℃. Thus, $La_{0.8}Sr_{0.2}CoO_3$ and $La_{0.8}Sr_{0.2}MnO_3$ were obtained as perovskite type oxides, and $ErBa_2Cu_3O_7$ and $YBa_2Cu_3O_7$ as oxide-superconductors.

Reaction was carried out in the tubular flow reactor and the products were analyzed by a gas chromatograph using Porapak T and activated carbon as column materials. Formaline solution consisting of 37 wt% formaldehyde, 7 wt% methanol, and 56 wt% H_2O was introduced through a micro-feeder into the air stream and was vaporized by the heating coil wound around the line. This gas mixture was fed into a reactor of 1/4-inch quartz tube. The temperature was measured and controlled by a CA thermocouple inserted into the 100 mg catalyst bed. The reaction products were directly introduced into the gas chromatograph by a sampling valve. Precise analysis of 0.1 mole% HCHO and CH_3OH was so difficult in this laboratory that a feed gas mixture was made as given in Table 1. 1.21 mole% HCHO used in this work is of exceedingly higher concentration than 0.1 mol%, an expected concentration of HCHO in the exhaust gas from methanol-

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Table 1. Composition of reactant gas mixture

Components	mole%
HCHO	1.21
CH_3OH	0.21
H_2O	3.04
N_2	75.47
O_2	20.06

Table 2. Surface area of the various catalysts

Catalysts	Treatment temp. (°C)	Surface area (m^2/g)
$La_{0.8}Sr_{0.2}CoO_3$	650	8.42
	800	4.71
	900	4.86
$La_{0.8}Sr_{0.2}MnO_3$	650	23.73
	800	7.23
	900	5.01

fueled vehicle. WHSV was kept at 50240 ml/h·g-cat.

RESULTS AND DISCUSSION

The crystallinity of La-based perovskites was conformed by XRD analysis. The XRD peaks of perovskite calcined at 650°C were slightly smaller than those calcined at 800°C or 900°C. This implies that the crystallinity of perovskites calcined at 650°C is imperfect. However, the crystallinity of perovskites calcined at 800°C or 900°C was the same with XRD peaks in the literature [6]. The crystallinity of $YBa_2Cu_3O_7$ was formed from 800°C.

The surface area of La-based perovskite measured by the BET method was given in Table 2. The surface area generally decreased with the increase in calcination temperature. Exceptionally, the surface area of $La_{0.8}Sr_{0.2}CoO_3$ calcined at 800°C was almost same with that calcined at 900°C. In general, the surface area of Mn-substituted perovskites was larger than the Co-substituted one at the same calcination temperature.

Fig. 1 exhibited the effect of the thermal treatment on the catalytic activity for the total oxidation of formaldehyde over $La_{0.8}Sr_{0.2}CoO_3$ and $La_{0.8}Sr_{0.2}MnO_3$, respectively. Fig. 2 exhibited the effect of the thermal treatment on the catalytic activity for the total oxidation of methanol over $La_{0.8}Sr_{0.2}CoO_3$ and $La_{0.8}Sr_{0.2}MnO_3$, respectively. It is presumed from these results that the catalytic activity is closely related to the calcination temperature and the specific surface area of the catalysts [6-8]. The catalysts calcined at the lower temperature have the larger specific surface area and hence give the higher activity. Comparing the catalytic activ-
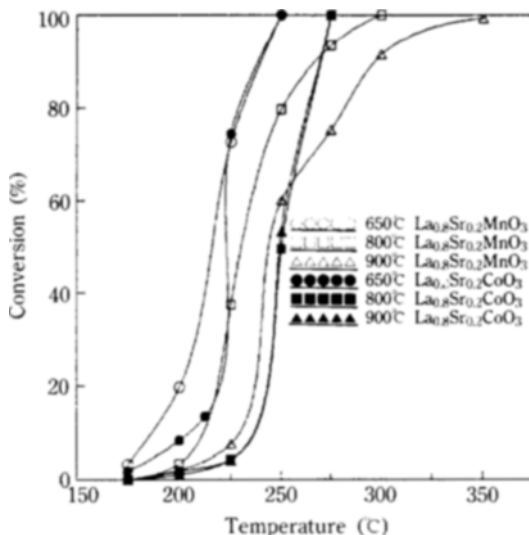

Fig. 1. Effect of calcination temperature on catalytic oxidation of HCHO over $La_{0.8}Sr_{0.2}MnO_3$ and $La_{0.8}Sr_{0.2}CoO_3$.
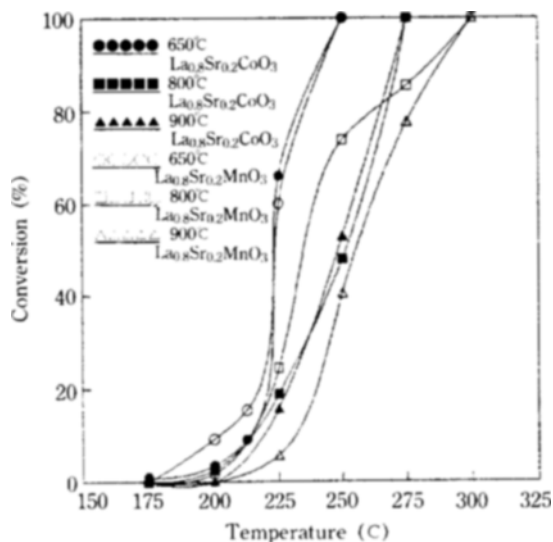

Fig. 2. Effect of calcination temperature on catalytic oxidation of CH_3OH $La_{0.8}Sr_{0.2}CoO_3$ and $La_{0.8}Sr_{0.2}MnO_3$.

ity of $La_{0.8}Sr_{0.2}CoO_3$ calcined at 650°C with that of $La_{0.8}Sr_{0.2}MnO_3$ calcined at the same temperature, Mn substituted perovskite shows better activity than the Co substituted one. This is believed to be resulted from the surface area of $La_{0.8}Sr_{0.2}MnO_3$ being 3 times that of $La_{0.8}Sr_{0.2}CoO_3$. However, for the same catalysts calcined at 800°C and 900°C, their catalytic activity is re-
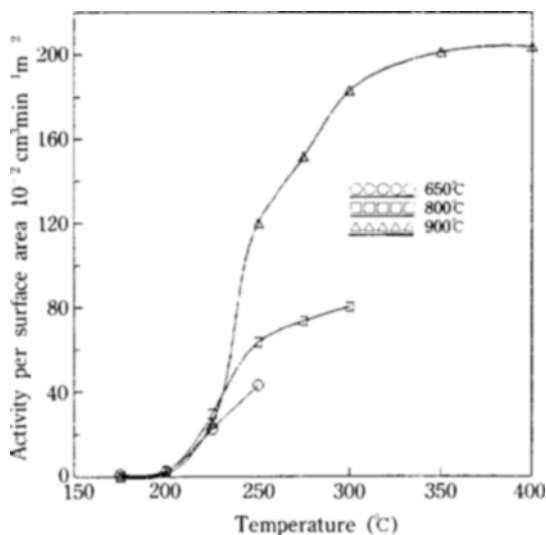
Fig. 3. Effect of calcination temperature on catalytic oxidation of HCHO over $La_{0.8}Sr_{0.2}MnO_3$ per surface area.
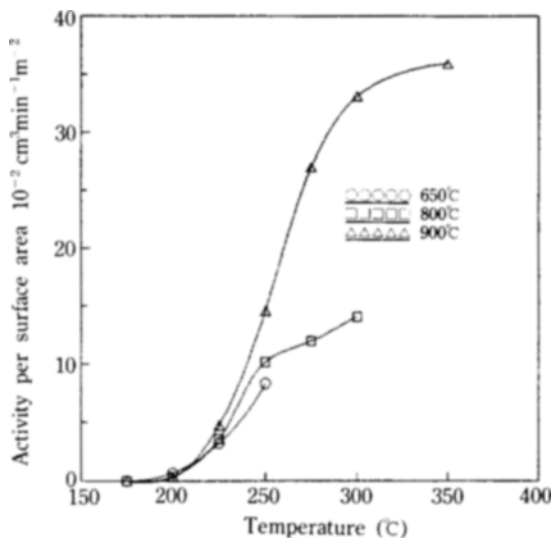

Fig. 4. Effect of calcination temperature on catalytic oxidation of CH_3OH over $La_{0.8}Sr_{0.2}MnO_3$ per surface area.

versed. According to a previous report [6]. since Mn^{+4} ion in $La_{0.8}Sr_{0.2}MnO_3$ is more stable than Co^{+4} ion in $La_{0.8}Sr_{0.2}CoO_3$, the oxidation over $La_{0.8}Sr_{0.2}MnO_3$ is conducted not only by the redox mechanism of the lattice oxygen but also partly by the adsorbed oxygen. Hence, the oxidation over $La_{0.8}Sr_{0.2}MnO_3$ is slower than that over $La_{0.8}Sr_{0.2}CoO_3$. For both catalysts, the catalytic activity based on the unit mass of the catalyst increases as the calcination temperature decreases, because the surface area of the catalysts increases with the decrease in calcination temperature. However, in terms of turnover frequency (TOF), the catalytic activity increases with the increase in calcination temperature, as exhibited in Fig. 3 and Fig. 4. This is because pure phase perovskite structure is readily formed as the calcination temperature becomes higher.

Fig. 5 represents the catalytic activity for the total oxidation of formaldehyde over $ErBa_2Cu_3O_{7-x}$ and $YBa_2Cu_3O_{7-x}$ along with the reaction temperature. The catalytic activity of both catalysts increased with the increase of reaction temperature. However, $ErBa_2Cu_3O_{7-x}$ exhibited 100% conversion at 350°C, while on $YBa_2Cu_3O_{7-x}$ 98% conversion was attained at 400°C. The reason that $ErBa_2Cu_3O_{7-x}$ showed better activity than $YBa_2Cu_3O_{7-x}$ is presumed to be resulted from the rapid electron transfer between the reactants and the catalyst, because the resistance of $ErBa_2Cu_3O_{7-x}$ is 1/10 of that of $YBa_2Cu_3O_{7-x}$ in the temperature range of 0-900°C [9].

Fig. 5. Catalytic oxidation of HCHO over $YBa_2Cu_3O_7$ and $ErBa_2Cu_3O_7$.

Mitchell et al. [4] reported that 0.02% HCHO was 100% converted on 0.054 wt% Pt/γ-Al_2O_3 at 227°C and at the space velocity of 52000 h^{-1}. In this work, $La_{0.8}Sr_{0.2}MnO_3$ and $La_{0.8}Sr_{0.2}CoO_3$ calcined at 650°C exhibited 100% conversion for 1.21% HCHO at 237°C and 250°C, respectively and at the space velocity of 50240 h^{-1}. As a result, La-based perovskite catalysts can be used for the treatment of exhaust gases from the methanol-fueled vehicle, since methanol has negligible amounts

of sulfur content.

CONCLUSION

The calcination temperature of $La_{0.8}Sr_{0.2}BO_3$ (B = Mn or Co) significantly influences the extent of the crystallinity as well as the surface area of the perovskites, and thus the catalytic activity for the total oxidation of formaldehyde and methanol. The lower is the calcination temperature, the higher is the surface area and thus the higher the catalytic activity, based on the unit mass of the catalyst. In terms of turnover frequency, however, the catalytic activity increases with the increase in calcination temperature, that is, it depends on the extent of the crystallinity of perovskite. Superconductive oxides such as $ErBa_2Cu_3O_{7-x}$ and $YBa_2Cu_3O_{7-x}$ shows rather lower catalytic activity for the total oxidation of formaldehyde than La-based perovskites.

ACKNOWLEDGEMENT

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