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Simultaneous removal of NO and carbon particulates over lanthanoid perovskite-type catalysts

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Abstract

The simultaneous removal of carbon particulate and NO_x has been studied over perovskite-type oxides prepared by malic acid method. The catalysts were modified to enhance the activity by substitution of metal into A- or B-site of perovskite oxide. In the $LaCoO_3$ catalyst, the partial substitution of Cs into A-site enhanced the catalytic activity in the combustion of soot particulate and NO reduction. In $La_{1-x}Cs_xCoO_3$ catalysts, the ignition temperature of carbon particulate decreases with increasing x values and shows almost constant values at substitution of $x > 0.2$ and NO conversion also shows the similar tendency. In the Cs-substituted oxide, the ignition temperature of carbon particulate slightly decreased in the order Co > Mn > Fe of B-site metal cation but NO conversion showed almost similar values. With increasing NO concentration, NO conversion decreased but the ignition temperature moved to high temperature when the NO concentration was higher than 1000 ppm. The carbon particulate played an important role on the reduction of NO, but NO had little effect on the oxidation of carbon particulate. © 2000 Published by Elsevier Science B.V.

Keywords: Carbon particulate; NO_x; Perovskite oxide

1. Introduction

Recently, the interest in diesel exhaust gas cleaning has increased significantly. Nitrogen oxides (NO_x) and soot particulates emitted from diesel exhaust have been causing severe environmental and health problem. Due to their small size, soot particulates can penetrate into the lung and they can form a serious health problem because of the presence of adsorbed hydrocarbons on their surfaces [1,2]. In addition, nitrogen oxides are major air pollutants that cause photochemical smog formation and acid rain [3].

Since the simultaneous reduction of NO_x and soot particulate emissions cannot be accomplished by engine modifications alone, catalytic processes for reducing the emission of both harmful substances should be developed [4–6]. As one promising process to meet this demand, Yoshida et al. [7] proposed the catalytic process by which both NO_x and soot particulates were removed simultaneously by using a soot trap loaded with CuO-based catalyst. Although this method involves many technological difficulties to be overcome, the development of active catalysts is considered to be most important. We have already studied the removal of NO and catalytic combustion of carbon particulate over perovskite-type oxides prepared by malic acid method [8–10].

In this study, several kinds of perovskite-type oxides were prepared by malic acid method, and their physical properties were characterized. We have also examined the catalytic activity for simultaneous removal of NO and carbon particulates in the presence of oxygen. In addition, we have examined the catalytic activity of modified perovskite-type oxides on the effect of

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reaction conditions, such as reaction temperature and NO concentration.

2. Experimental

The preparation method of perovskite-type oxides was followed by previous paper [8]. Malic acid was added into mixed aqueous solution of metal nitrates in a desired proportion so as for the molar ratio of malic acid to the total metal cations to be unity. The solution was then evaporated to dryness with stirring, and further dried at 150°C. The precursor was ground and then calcined in air at 200°C for 30 min, 350°C for 30 min and 600°C for 12 h. The calcination temperature was determined by the result of thermal analysis of precursors.

Experiments were performed with a model carbon (Printex-U) which was obtained from Degussa AG. Properties of this model carbon have been described in detail [11]. Properties (primary particle size, BET surface area, oxidation rate) of this model soot are similar to those of the real diesel soot particulate. The catalyst and the soot (5 wt.%) were well mixed in an agate mortar with a pestle for more than 20 min. Although the soot/catalyst contact is known to significantly affect the results [11], this mixing procedure gave reproducible results under the present experimental conditions. The catalyst/soot mixture (0.2 g) was placed in a quartz-tube reactor and, after the pretreatment at 300°C for 2 h and cooling down to 200°C in a He stream, the temperature programmed reaction (TPR) was started with the linear heating rate of 1°C/min in a gaseous mixture of O_2 (4%), NO (5000 ppm) and He (balance) (flow rate: 100 cm^3/min). The outlet gases were analyzed by gas chromatography (HP 5890) and NO_x analyzer (Mapo Technomax) at intervals of about 20 min. The soot was almost oxidized into CO_2 and very small amount of CO was detected but it was neglected. In addition, the carbon mass balances were generally better than 97%.

The crystal structures of prepared oxides were examined by powder X-ray diffraction (XRD) with Cu Kα radiation (Rigaku Model DMax) and the BET surface area was measured using BET measuring apparatus (Quanta Chrome Surface Area Analyzer).

3. Results and discussion

3.1. Characterization of catalyst

The thermogravimetric analysis of catalyst/carbon mixture was carried out in order to elucidate the combustion property of carbon particulate with catalyst. While non-catalytic oxidation of soot particulates occurred around 500°C, the ignition temperature remarkably decreased in the presence of catalyst. Especially, it decreased more than 200°C over $La_{0.6}Ce_{0.4}CoO_3$ catalyst and the soot was completely oxidized around 400°C. This suggests that the catalyst promote the oxidation rate of carbon particulates.

The crystal structures of prepared oxides were examined by XRD. XRD patterns showed large peak at 33° and confirmed the formation of perovskite crystalline phase [12]. The surface area of perovskite oxides was measured by BET measuring apparatus. More than 20 m^2/g surface area was obtained in the catalyst prepared by malic acid method.

3.2. Simultaneous removal of NO and carbon particulate

The carbon removal reaction supposedly takes place at the two-phase boundary of a solid catalyst, a solid reactant (carbon particulate) and gaseous reactants (O_2, NO). Because of the experimental difficulty to supply the solid carbon continuously to the reaction system, the reaction have been exclusively investigated by the TPR technique in which a mixture of a catalyst and a soot is heated in gaseous reactants [13].

Fig. 1 shows a typical result of TPR over $La_{0.6}Ce_{0.4}CoO_3$ catalyst. The formation of carbon dioxide due to oxidation of the carbon particulate and the reduction of NO were observed at the similar temperature range. The curves of carbon dioxide formation and NO conversion were very similar in shape. This result suggests the possibility of the simultaneous removal of NO and carbon particulate. The sharp drop of carbon dioxide formation at temperature higher than 320°C is undoubtedly due to the exhaustion of the charged carbon particulate. Within the rising portion of carbon dioxide formation curve, the sufficient amount of the charged carbon particulate still remains.

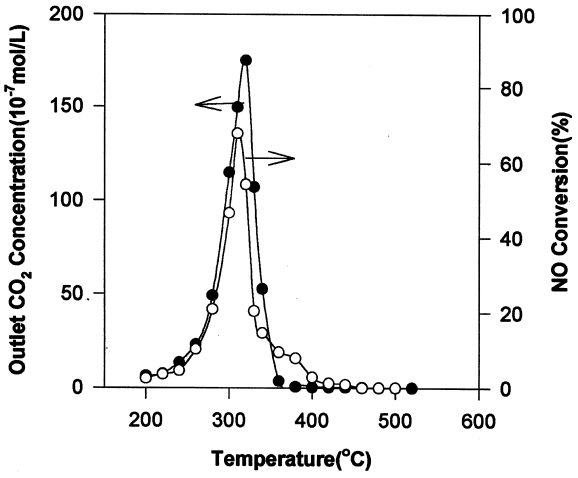

Fig. 1. TPR of the simultaneous removal of NO and carbon particulate over $La_{0.6}Cs_{0.4}CoO_3$ catalyst: heating rate = 1 K/min, NO = 1000 ppm, O_2 = 4%.

Fig. 2 shows outlet CO_2 concentration over $La_{0.6}Ce_{0.2}Cs_{0.2}CoO_3$ catalyst at the various reactants composition. In the absence of oxygen (Fig. 2(a)), carbon dioxide is produced at very high temperature, which is thought to be due to the carbon particulate oxidation by lattice oxygen. The similar tendency was shown with the previous report in the presence of catalyst and carbon particulate [10]. In the absence of catalyst (Fig. 2(b)), similar curve is obtained. It is thought that NO is decomposed thermally and the produced oxygen is subsequently used as an oxidant in the oxidation of carbon particulate at higher temperature.

In the presence of NO and oxygen (Fig. 2(c)), outlet CO_2 concentration goes through a maximum at about 300°C and similar result is obtained in the absence of NO (Fig. 2(d)). It demonstrates that NO has little effect on the catalytic oxidation of carbon particulate.

Fig. 3 shows the temperature dependence of NO conversion over $La_{0.6}Ce_{0.2}Cs_{0.2}CoO_3$ catalyst at the various reactants composition. In the absence of catalyst (Fig. 3(a)), no NO is reduced at lower temperature and small amount of NO is decomposed at higher temperature. This result suggests that perovskite-type oxides catalyze the reduction of NO effectively. In the absence of oxygen (Fig. 3(b)), NO is gradually reduced with increasing temperature and completely decomposed above 400°C. As was reported in the previous work [8], it is confirmed that oxygen is necessary for the reduction of NO over perovskite oxide. However, CO_2 and N_2 can be formed by the following carbon–NO reaction without oxygen:

$$C + 2NO \rightarrow CO_2 + N_2$$

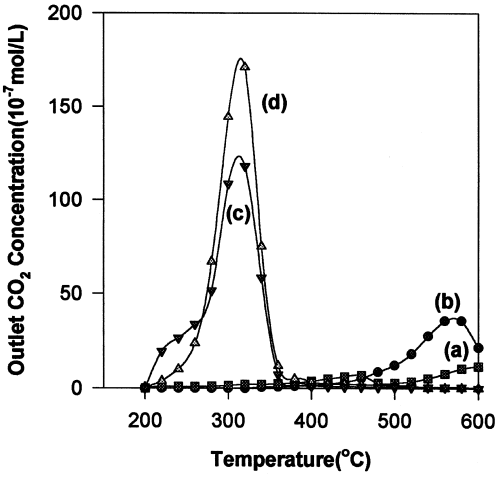

Fig. 2. Outlet CO_2 concentration during TPR over $La_{0.6}Ce_{0.2}Cs_{0.2}CoO_3$ at the various reaction conditions: NO = 600 ppm, O_2 = 4%: (a) carbon + NO + catalyst; (b) carbon + O_2 + NO; (c) carbon + O_2 + NO + catalyst; (d) carbon + O_2 + catalyst.

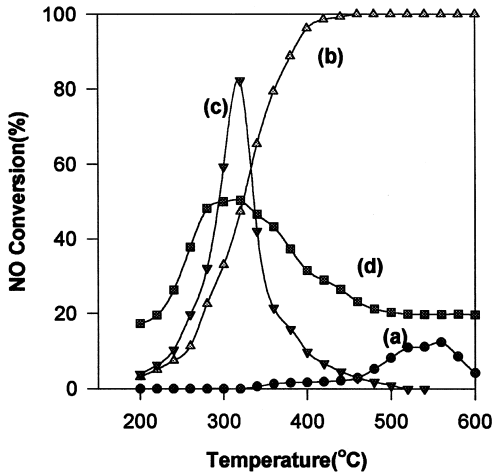

Fig. 3. NO conversion during TPR over $La_{0.6}Ce_{0.2}Cs_{0.2}CoO_3$ at various reaction conditions: NO = 1000 ppm, O_2 = 4%: (a) NO + carbon + O_2; (b) NO + carbon + catalyst; (c) NO + carbon + catalyst + O_2; (d) NO + catalyst + O_2.

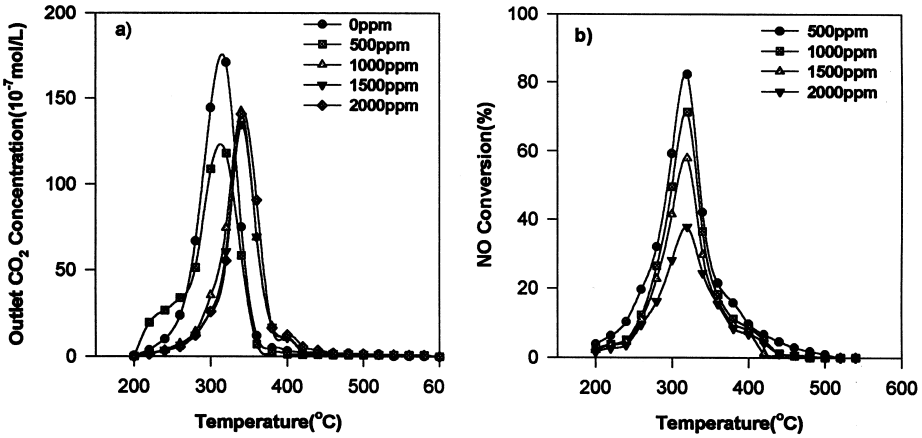

Fig. 4. Outlet CO_2 concentration (a) and NO conversion (b) during TPR over $La_{0.6}Ce_{0.2}Cs_{0.2}CoO_3$ at the various NO concentrations: heating rate = 1 K/min, O_2 = 4%.

It is well known that oxygen ion moves through the lattice vacancy in the perovskite-type oxides [14]. Accordingly the oxygen vacancies increase owing to the continuous removal of oxygen by reducing agent at the surface as the mobility of oxygen ion increases in the lattice. From the TPR results in the previous study [8], the lattice oxygen is easily removed at about 400°C. Therefore NO is easily adsorbed on the oxygen vacancy site of catalyst above 400°C and then gives rise to the formation of CO_2 and N_2 by reacting with carbon particulate. This is consistent with the result reported by Teraoka and coworkers [15].

In the presence of NO and oxygen (Fig. 3(c)), NO conversion has the maximum value at about 300°C and then drops sharply owing to exhaustion of the charged carbon particulate at higher temperature. This result indicates that carbon particulate plays an important role on the reduction of NO. In the absence of carbon particulate (Fig. 3(d)), NO conversion curve shows also maximum value at about 300°C but the maximum value is lower when compared with the value in the presence of carbon particulate. In addition, NO is still decomposed above 400°C, even though it is small. This curve is shown to have very similar shape with the previous work of NO reduction over $La_{0.6}Ba_{0.4}CoO_3$ catalyst [8].

In carbon–O_2–NO reaction, the formations of CO_2 and N_2 are observed. Fig. 4 shows the temperature dependence of outlet concentration of CO_2 and the temperature dependence of NO conversion at various NO concentration over $La_{0.6}Ce_{0.2}Cs_{0.2}CoO_3$ catalyst.

In the absence of NO, the ignition temperature of carbon particulate which is estimated by extrapolating the steeply ascending linear portion of carbon dioxide formation curve to zero carbon dioxide concentration is relatively low. In addition, the ignition temperature shows almost the same value in the NO concentration of 500 ppm. On the contrary, the ignition temperature moves to high temperature in the NO concentration higher than 1000 ppm. It may be thought that NO occupies the active site of catalyst surface predominantly at high NO concentration and then prohibits the reaction of carbon particulate on the catalyst surface.

The NO conversion increases with decreasing NO concentration and all the curves show almost the same pattern. This result is consistent with the previous work in the absence of carbon particulate [8]. However, NO conversion shows higher value in comparison in the absence of carbon particulate. In the real condition of diesel exhaust gas, the outlet NO concentration is known to be about 500 ppm. Therefore it is thought that the simultaneous removal of NO and soot particulate will be successfully carried out on the perovskite-type oxide.

From the preceding results, it is confirmed that carbon particulate plays an important role on the reduction of NO as reducing agent, but NO has little effect on the oxidation of carbon particulate. On the

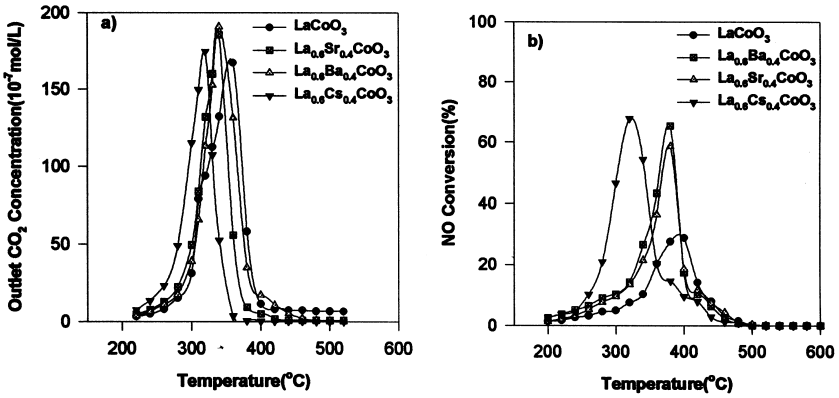

Fig. 5. Outlet CO_2 concentration (a) and NO conversion (b) during TPR over various perovskite oxides: heating rate = 1 K/min, NO = 1000 ppm, O_2 = 4%.

contrary, NO retards the oxidation of carbon particulate at high concentration of NO. Anyway, the formation of carbon dioxide is controlled not by NO concentration but by oxygen concentration, because NO is introduced into reactants in a very small amount compared to oxygen. In the carbon–O_2 reaction, it is reported that carbon particulate is oxidized by adsorbed oxygen on the catalyst surface [10]. Gaseous oxygen is adsorbed dissociatively on the catalyst surface and then the resulting O_{ad} species attack the reactive free carbon to give an oxygen-containing active intermediate. Finally, the reaction between active intermediate and O_{ad} or gaseous oxygen produces CO_2. The following reaction mechanism can be proposed from preceding results [10]:

$$O_2\,(g) \leftrightarrow 2O_{ad}$$

$$C + O_{ad} \rightarrow C^*[O]$$

$$C^*[O] + O_{ad} \rightarrow CO_2\,(g)$$

$$C^*[O] + \tfrac{1}{2}O_2 \rightarrow CO_2\,(g)$$

In the carbon–NO reaction, carbon plays a role of reducing agent in the reduction of NO. The adsorbed NO on catalyst surface attacks the reactive carbon particulate to give reactive surface carbon complex and then the resulting carbon complex is decomposed to N_2 and CO_2 by the following reaction [15]:

$$NO\,(g) \rightarrow NO_{ad}$$

$$NO_{ad} + C \rightarrow C^*[N, O]$$

$$C^*[N, O] + NO_{ad} \rightarrow CO_2\,(g) + N_2$$

In the NO–oxygen reaction, it is reported that NO is easily oxidized to NO_2 in the presence of oxygen [16]. The resulting NO_2 is dissociatively adsorbed on the catalyst surface to form adsorbed O_{ad} and NO_{ad} species.

It is suggested that carbon particulate is directly oxidized by gaseous oxygen or adsorbed oxygen to give CO_2 and also accelerates the reduction of NO to give a reactive carbon–NO complex by reacting with adsorbed NO on catalyst surface.

3.3. Effect of substitution of metal ion

The catalytic performance of perovskite-type oxides is significantly changed by the modification of both A- and B-site cations, and it is convenient to discuss the effect of A- and B-site cations separately in order to verify the effect of oxide composition on the catalytic activity.

Fig. 5 shows the effect of substitution of metal cation into A-site of $LaCoO_3$ on the temperature dependence of outlet CO_2 concentration and NO conversion. The substitution of Cs into A-site of $LaCoO_3$ lowers the ignition temperature of carbon particulate. However, the substitution of Ba and Sr shows little change in the ignition temperature compared to $LaCoO_3$ catalyst, while they showed high activity on the reduction of NO in the previous study [8].

From the previous TPR results [8], the lower temperature peak area of $La_{0.6}Cs_{0.4}CoO_3$ appeared larger than that of other catalysts. It was also reported that the substitution of monovalent alkali metal ion for trivalent La^{3+} brings about the formation of oxide ion vacancy site or the oxidation of B-site cations [11]. In addition, from the simple geometric consideration, unit cells should expand by the substitution of large alkali metal ion for smaller lanthanum. These results suggest that the alkali ion substitution of $LaCoO_3$ increases the activity of carbon oxidation. Accordingly the substitution of Cs gives rise to easy reduction of oxides and forms oxide ion vacancies of surface and then increases the adsorption rate of active oxygen at catalyst surface.

In addition, this result shows almost same tendency with the previous work in the absence of NO [10]. From these results, it is suggested that NO has little effect on the oxidation of carbon particulate. Therefore the catalytic oxidation of carbon particulate is usually dependent on the property of perovskite-type oxide.

The substitution of Cs into A-site of $LaCoO_3$ increases the NO conversion and the curve moves to lower temperature. In addition, the substitution of Ba or Sr into A-site of $LaCoO_3$ also increases the NO conversion. This result coincides well with the previous work [8]. In the substitution of Cs into A-site of $LaCoO_3$, the maximum outlet CO_2 concentration appears at the same temperature range of maximum NO conversion. In the substitution of Ba or Sr into A-site of $LaCoO_3$, the maximum outlet CO_2 concentration appears at a little low temperature range of maximum NO conversion. In addition, NO conversion drops to zero at higher temperature range over all catalysts due to the exhaustion of the charged carbon particulate. It is repeatedly confirmed that carbon particulate plays an important role on the reduction of NO.

Fig. 6 shows the effect of substitution of Cs cation into A-site of $LaCoO_3$ on the temperature dependence of outlet CO_2 concentration and NO conversion.

In the $La_{1-x}Cs_xCoO_3$ catalyst, the ignition temperature decreases with increasing x values and shows an almost constant values upon substitution of $x > 0.2$. This result shows almost same tendency with the previous work in the absence of NO [10]. It is thought that the oxygen vacancy sites of perovskite oxide increase with increasing amount of Cs and then the oxidation activity also increases. This result is also verified by the previous TPR result of these catalysts [8].

In addition, the NO conversion increases with increasing x values and shows an almost constant values upon substitution $x > 0.2$. In the $La_{1-x}Cs_xCoO_3$ catalyst, the maximum outlet CO_2 concentration also appears at the same temperature range of maximum NO conversion.

In the Cs-substituted oxides, the effect of substitution of B-site is observed. Fig. 7 shows the effect of substitution of B-site on the temperature dependence of outlet CO_2 concentration and NO conversion.

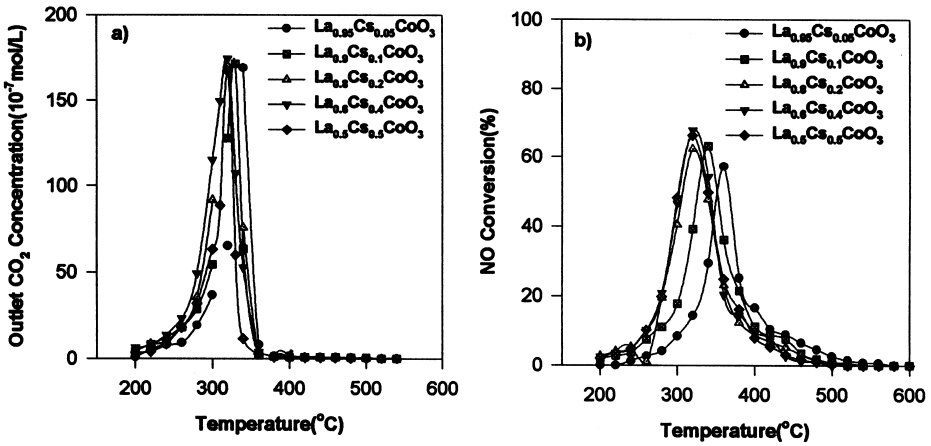

Fig. 6. Outlet CO_2 concentration (a) and NO conversion (b) during TPR over $La_{1-x}Cs_xCoO_3$ catalysts: heating rate = 1 K/min, NO = 1000 ppm, O_2 = 4%.

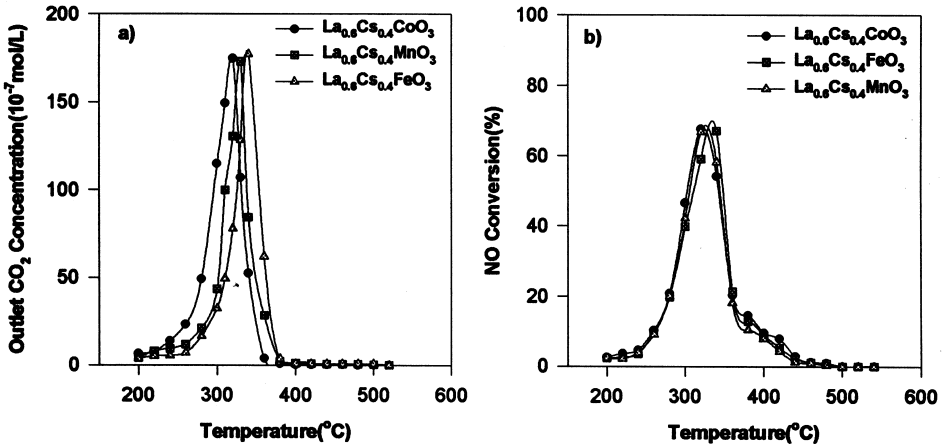

Fig. 7. Outlet CO_2 concentration (a) and NO conversion (b) during TPR over various perovskite oxides: heating rate = 1 K/min, NO = 1000 ppm, O_2 = 4%.

The ignition temperature of carbon particulate slightly decreases in the order Co > Mn > Fe. The catalytic activity for gas-phase oxidation reactions of Co- and Mn-based perovskite-type oxides is known to be higher than that of Fe-based perovskites [17]. Judging from ignition temperature, this activity order with respect to the B-site cations is also true in the present carbon–NO–oxygen reaction. This ignition temperature, however, is not significantly changed in comparison to substitution of A-site of $LaCoO_3$ catalyst.

The NO conversion shows almost same values over all the catalyst, but the curve moves to high temperature range on the Fe-based perovskite. In the previous work, however, NO conversion is strongly affected by the substitution of metal cation into B-site in the absence of carbon particulate [8].

These results may indicate that it is difficult to promote the catalytic performance for the simultaneous removal of NO and carbon particulate solely by the change of B-site composition. NO conversion depends strongly on the carbon particulate rather than the property of catalyst in the presence of carbon particulate.

4. Conclusions

The simultaneous catalytic removal reaction of carbon particulate and NO over perovskite-type oxides was performed. In the $LaCoO_3$-type perovskite oxide, the partial substitution of Cs into A-site enhanced the oxidation rate of carbon particulate and NO conversion. In $La_{1-x}Cs_xCoO_3$ catalysts, the ignition temperature of carbon particulate decreases with increasing x values and shows almost constant values at substitution of $x > 0.2$ and NO conversion also shows the similar tendency. In the Cs-substituted oxide, the ignition temperature of carbon particulate slightly decreases in the order Co > Mn > Fe of B-site metal cation but NO conversion showed almost similar values. With increasing NO concentration, NO conversion decreased but the ignition temperature moved to high temperature in the NO concentration more than 1000 ppm. The carbon particulate played an important role on the reduction of NO.

Acknowledgements

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