Simultaneous Catalytic Removal of NO and Carbon Particulates Over Perovskite-type Oxides

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Abstract: We have studied the simultaneous removal of carbon particulate and NOx 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 LaCoO3 catalyst, the partial substitution of Cs into A-site enhanced the catalytic activity in the combustion of soot particulate and NO reduction. 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.

Keywords: Carbon Particulate, NOx, Perovskite Oxide.

1. Introduction

Recently the interest in diesel exhaust gas cleaning has increased significantly. Diesel engine powered vehicles are a major source for the emission of soot particulates and NOx in urban areas. 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 NOx 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 and coworkers [7] proposed the catalytic process by which both NOx and soot particulates were removed simultaneously by using a soot trap loaded with CuO-based catalyst. In this method, the development of active catalysts is considered to be of primary importance, though there are many technological difficulties to be overcome such as the development of efficient and thermally stable traps and the enhancement of contact between catalyst and trapped soot. 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].

Perovskite type oxides, which are structurally similar to the mineral of that name (CaTiO3), have long been studied because of technologically important characteristics. In 1971, cobaltate perovskites were suggested as substitutes for noble metal in automotive exhaust catalyst [11].

In the present work, several kinds of perovskite-type oxides were prepared by malic acid method, and their 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 reaction conditions, such as reaction temperature, NO concentration and contact time.

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 pH of the mixed aqueous solution was controlled to be 4.0 by addition of ammonia water. 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 hrs. The calcination temperature was determined by the result of thermal analysis of precursors.

Experiments were performed with a model carbon mixture was carried out in order to elucidate the combustion property of carbon particulate with catalyst. While noncatalytic 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 \( \text{La}_0.6\text{Ce}_{0.4}\text{Co}_3 \) catalyst and the soot was completely oxidized around 400 °C. This suggests that the catalyst promotes the oxidation rate of soot 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 [13].

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
Simultaneous Catalytic Removal of NO and Carbon Particulates Over Perovskite-type Oxides

Figure 1. Temperature programmed reaction of the simultaneous removal of NO and carbon particulate over La$_{0.6}$Ce$_{0.4}$Co$_3$O$_7$ catalyst: heating rate = 1 K/min, O$_2$ = 4%, NO = 1000 ppm.

Figure 2. Outlet CO$_2$ concentration during temperature programmed reaction over La$_{0.6}$Ce$_{0.4}$Co$_3$O$_7$ at the various reaction conditions: NO = 600 ppm, O$_2$ = 4%, a) carbon+NO+ catalyst, b) carbon+O$_2$+NO, c) carbon+NO+O$_2$+catalyst, d) carbon+O$_2$+catalyst.

produced oxygen is subsequently used as an oxidant in the oxidation of carbon particulate at higher temperature.

In the presence of NO and oxygen(Figure 2(c)), outlet CO$_2$ concentration goes through a maximum at about 300 °C and similar result is obtained in the absence of NO(Figure 2(d)). It demonstrates that NO has little effect on the catalytic oxidation of carbon particulate.

Figure 3 shows the temperature dependence of NO conversion over La$_{0.6}$Ce$_{0.4}$Co$_3$O$_7$ catalyst at the

Figure 3. NO conversion during temperature programmed reaction over La$_{0.6}$Ce$_{0.4}$Co$_3$O$_7$ at various reaction conditions: NO = 1000 ppm, O$_2$ = 4%, a) without catalyst, b) without O$_2$, c) with carbon+catalyst+O$_2$, d) without carbon.

various reactants composition.

In the absence of catalyst(Figure 3(a)), NO is thermally decomposed at higher temperature and this result suggests that perovskite-type oxides catalyze the reduction of NO effectively. In the absence of oxygen(Figure 3(b)), NO is gradually decomposed as 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.

\[ C + 2NO \rightarrow CO_2 + N_2 \]

It is well known that oxygen ion moves through the lattice vacancy in the perovskite-type oxides [15]. 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 [4], 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 formation of CO$_2$ and N$_2$ by reacting with carbon particulate. This is consistent with the result reported by Teraoka and coworkers [16].

In the presence of NO and oxygen(Figure 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 (Figure 3(d)), NO conversion curve shows also maximum value at about 300 °C but the maximum value is lower when compared with the 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$_{0.8}$Ba$_{0.2}$CoO$_3$ catalyst [8].

In carbon-O$_2$-NO reaction, the formations of CO$_2$ and N$_2$ are observed. Figure 4 shows the temperature dependence of outlet concentration of CO$_2$ over La$_{0.8}$Ce$_{0.2}$Cs$_{0.2}$CoO$_3$ catalyst at the various NO concentration.

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 adsorption of carbon particulate on the catalyst surface.

Figure 5 shows the temperature dependence of NO conversion over La$_{0.8}$Ce$_{0.2}$ Cs$_{0.2}$CoO$_3$ catalyst at the various NO concentration.

The NO conversion increases with decreasing NO concentration and all the curves shows 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 with the absence of carbon particulate. In the real condition of diesel exhaust gas, the outlet NO concentration is known as 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 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].
Simultaneous Catalytic Removal of NO and Carbon Particulates Over Perovskite-type Oxides

\[
\begin{align*}
O_2(g) & \leftrightarrow 2O_{ad} \\
C + O_{ad} & \rightarrow C[O] \\
C[O] + O_{ad} & \rightarrow CO_2(g) \\
C[O] + \frac{1}{2}O_2 & \rightarrow CO_2(g)
\end{align*}
\]

In the carbon-NO reaction, carbon plays a role of reducing agent on 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 [16].

\[
\begin{align*}
NO(g) & \rightarrow NO_{ad} \\
NO_{ad} + C & \rightarrow C[NO] \\
C[NO] + NO_{ad} & \rightarrow CO_2(g) + N_2
\end{align*}
\]

In the NO-oxygen reaction, it is reported that NO is easily oxidized to NO\(_2\) in the presence of oxygen [17]. The resulting NO\(_2\) is dissociatively adsorbed on the catalyst surface to form adsorbed O\(_{ad}\) and NO\(_{ad}\) species. However, the amount of O\(_{ad}\) species formed from NO\(_2\) is much smaller than O\(_{ad}\) species formed from gaseous oxygen.

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.

Figure 6 shows the effect of substitution of metal cation into A-site of LaCoO\(_3\) on the temperature dependence of outlet CO\(_2\) concentration.

The substitution of Cs into A site of LaCoO\(_3\) lowers the ignition temperature of carbon particulate. However, the substitution of Ba or 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 [4], the lower temperature peak area of La\(_{0.9}\)Cs\(_{0.1}\)CoO\(_3\) appeared larger than that of other catalysts. It was also reported that the substitution of monovalent alkali metal ion for tri-valent La\(^{3+}\) brings about the formation of oxide ion vacancy site or the oxidation of B-site cations [12]. 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.

Figure 7 shows the effect of substitution of metal into A-site of LaCoO\(_3\) on the temperature dependence of NO conversion.

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.

Figure 6. Outlet CO\(_2\) concentration during temperature programmed reaction over various perovskite oxides: heating rate = 1 K/min, NO = 1000 ppm, O\(_2\) = 4%.
that carbon particulate plays an important role on the reduction of NO.

In the Cs-substituted oxides, the effect of substitution of B-site is observed. Figure 8 shows the effect of substitution of B-site on the temperature dependence of outlet CO$_2$ concentration.

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 [18]. 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.

Figure 9 shows the effect of substitution of B-site on the temperature dependence of NO conversion.

The NO conversion shows almost same values over the all 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].

Thus 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 and NO conversion depends strongly on the carbon particulate rather than the property of catalyst in the presence of carbon particulate.

4. Conclusions

The following conclusions are drawn from the simultaneous removal reaction of carbon particulate and NO over perovskite-type oxides.

1) In the LaCoO$_3$ type perovskite oxide, the partial substitution of Cs into A-site enhanced oxidation rate of carbon particulate and NO conversion.

2) 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.

(3) With increasing NO concentration, NO conversion decreased but the ignition temperature moved to high temperature in the NO concentration more than 1000 ppm.

(4) The carbon particulate played an important role on the reduction of NO but NO had little effect on the oxidation of carbon particulate.

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