Reduction of lean NO₂ with diesel soot over metal-exchanged ZSM5, perovskite and γ-alumina catalysts

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Abstract−The catalytic performances of metal-exchanged ZSM5, perovskite and γ-alumina catalysts for the reduction of nitrogen dioxide (NO_2) by diesel soot were investigated. The reaction tests were performed through temperature-programmed reaction (TPR), in which NO_2 and O_2 were passed through a fixed bed of catalyst-soot mixture. On the three types of catalyst, NO_2 was reduced to N_2 by model soot (Printex-U) and most of the soot was converted into CO_2. Pt-, Cu- and Co-exchanged ZSM5 catalysts exhibited reduction activities with conversions of NO_2 into N_2 of about 20%. Among the perovskite catalysts tested, $La_{0.9}K_{0.1}FeO_3$ showed a 32% conversion of NO_2 into N_2. The catalytic activities of the perovskite catalysts were largely influenced by the number and stability of oxygen vacancies. For the γ-alumina catalyst, the peak reduction activity appeared at a relatively high temperature of around 500 °C, but the NO_2 reduction was more effective than the NO reduction, in contrast to the results of the ZSM-5 and perovskite catalysts.

Key words: Diesel Soot, Selective Catalytic Reduction, ZSM5, Perovskite, γ-Alumina

INTRODUCTION

In diesel emission aftertreatment, reducing the particulate matters (PM or soot) has received considerable attention in the attempts to satisfy emission standards. Current research has been focusing on self-regenerating catalytic filters as a promising answer to this problem [1-3]. The optimization of such catalytic filters is presently concentrated on finding the best catalyst material to oxidize soot under practical conditions [4,5]. Most studies have focused on developing catalysts to generate NO_2 from NO in diesel emissions, since NO_2 is very efficient in oxidizing carbon via the following two paths [2,5]:

$$NO_2 + C \rightarrow 1/2\,N_2 + CO_2 \qquad (1)$$

$$NO_2 + C \rightarrow NO + CO \qquad (2)$$
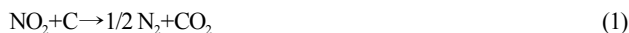
Of these, route (1) is more desirable than (2) because it not only combusts solid carbons but also reduces NOx into N_2, both of which are important for diesel exhaust aftertreatment.

Besides this on-site NO_2 production, NO_2 can be supplied directly to the filter system by using an oxidation catalyst [2,5,6] or plasma reactor [7,8] before the catalytic filter. If NO_2 can be produced or supplied at a sufficient level via such methods, a high rate of soot removal can be achieved by stimulating the oxidation of soot with NO_2. Thus, the search for an effective catalyst to promote reaction route (1) is a priority task in the field of self-regenerating catalytic filter. Nevertheless, the studies so far have mostly focused on the oxidation of soot under NO-O_2 environment, while very few studies have dealt with the soot combustion under a NO_2-O_2 environment [9,10].

About a decade ago, diesel soot was not generally accepted as a candidate for NOx reductant. However, Teraoka and colleagues have reported several studies [11-13] on NOx reduction with soot materials, which revealed that diesel soot could be used as a reductant for lean deNOx, especially in the presence of perovskite and spinel-type catalysts. (Perovskite catalyst is also known to remove NOx with hydrocarbon [14].) Because diesel soot contains 2.2 wt% of hydrogen on average, NOx reduction is possible only if the catalysts are tightly contacted with the soot [5,15]. Many studies have followed Teraoka's work concerning soot-NO-O_2 reaction under perovskite catalysts [15-22]. The studies generally suggested that the partial incorporation of 1A metal into an A-site element [12,15, 16,18-20] or a specific combination of B-site elements [12,15,21] were effective for soot oxidation with NO-O_2 over perovskite catalysts.

Zeolite catalysts have been intensively studied as hydrocarbon-SCR (selective catalytic reduction) catalysts [23-26] for years. Among various kinds of zeolite, metal-exchanged ZSM5 catalysts have been most frequently studied, since it is reported that Cu-ZSM5 is highly active toward NO reduction [27,28]. Zeolite catalysts were also applied to the soot combustion under the NO-O_2 environment [27-30].

γ-Alumina was reported to show high deNOx performance when NO_2 was fed as the NOx species [31,32]. This performance was also confirmed in a study about plasma-enhanced catalysis [33], where plasma was used to convert NO into NO_2 and alumina effectively reduced this NO_2 with hydrocarbons.

In this study, we investigated and compared the performances of lean NO_2 reduction with diesel soot under ZSM5, perovskite and γ-alumina catalysts. We checked the concentrations of N_2 and CO_2

for every reaction to determine the effectiveness of each catalyst's activity in promoting the reaction route (1). Soot-NO-O$_2$ reactions were also tested over the catalysts and the results were used to clarify the characteristics of the soot-NO$_2$-O$_2$ reaction. The perovskite catalysts were selected based on the results provided in Teraoka's studies [11,12].

EXPERIMENTAL

1. Preparation of Catalysts

In preparing the Pt-, Cu- and Co-exchanged ZSM5 catalysts, we used proton-type ZSM5 catalysts (PQ corporation) of SiO$_2$/Al$_2$O$_3$= 30. Metal acetates (Aldrich, 99%) were dissolved in deionized water to make 10 mmol/L aqueous solution. ZSM5 was poured into this solution and the slurry was maintained at 95 °C while stirred for 12 hours, after which it underwent washing with excessive deionized water, drying (110 °C, 12 hours) and calcination (550 °C, 4 hours). The exchanged amounts of metal were measured with ICP-AES (Jobin, Yvon 138 Ultrace). The measured wt% was tagged at the end of the material names. For example, Pt-ZSM5-53 means the catalyst containing 53 wt% of Pt.

For preparing the perovskite catalysts, nitrate precursors of constituted metals (Yakuri, 99%) were dissolved collectively in deionized water to make 0.25 mol/L solution for each precursor. Maleic acid (Aldrich, 99%) was added to the solution at an amount corresponding to the mol ratio of acid : total metal of 0.5 : 1. The solution was vacuum-evaporated at 90 °C for 3 hours and the resulting particles were decomposed at 350 °C for 4 hours. Final perovskite particles were obtained after air-calcination of the decomposed products at 850 °C for 10 hours.

The γ-alumina used in this study, purchased from Sumitomo Company, had a specific surface area of 156 m^2/g, total pore volume of 0.51 cc/g and average pore diameter of 131 Å.

2. Characterization of the Model Soot

Printex-U (Degussa) was used as a model material for diesel soot in this study. Through scanning electron microscopy (SEM) analysis, the average particle size of Printex-U was determined to be 0.25 μm. Because the average diameter of diesel soot is known to range from 0.01 to 2.5 μm, Printex-U was thought to meet the dimensional standard as a model soot.

The result of the elemental analysis (Carlo Erba E.A. 1108) is

Table 1. Elemental compositions of general diesel soot and the model soot used in this study

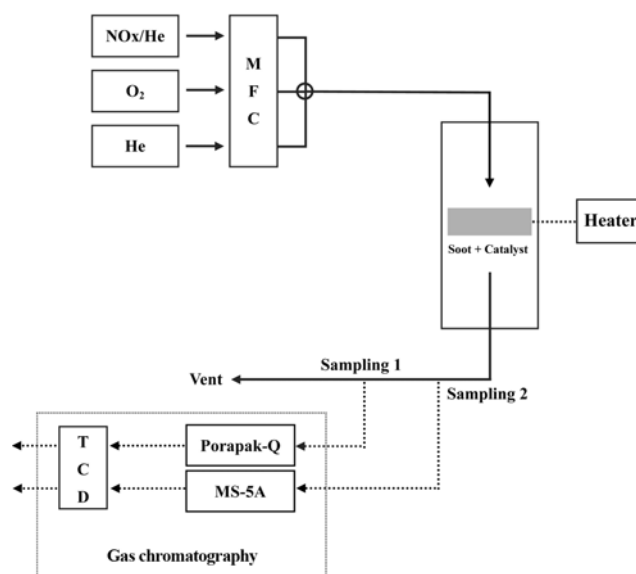| Sample	Element	Weight %
Diesel soot	C	80.7
	H	2.2
	N	0.6
	S	1.6
	O	14.8
Model soot (Printex-U)	C	93.3
	H	0.5
	N	0.3
	S	0.2
	O	3.7

Fig. 1. Schematic of instrumental set-up for the reaction tests.

presented in Table 1. Printex-U was compared with the real engine soot which was obtained from the tail pipe of 2 L diesel engine (D20, Hyundai). The hydrogen content in the model soot was 0.5 wt%. Considering that real diesel soot contains 2.2 wt% hydrogen on average, we considered Printex-U to be an acceptable model material for diesel soot, as it would not exaggerate the SCR activity of the tested catalyst any more than in the use of real diesel soot.

3. Instrumental Set-up and Reaction Test

Temperature-programmed reaction (TPR) was adopted as the reaction test procedure. The instrumental set-up is displayed in Fig. 1. NO$_2$ (or NO) gas at 1,980 ppm in helium balance (PS Chem) was used and mixed with oxygen (PS Cehm, 99.999%) and additional helium (PS Chem, 99.999%) to make a reaction gas consisting of 1,760 ppm NO$_2$ (or NO) and 5 (or 10) % O$_2$. The gas flow rates were controlled by mass flow controllers (MFC, Bronkhorst). The tubular reactor (1.1 cm i.d.) was made with Pyrex glass and a glass filter was positioned in the middle of the reactor. Catalyst and soot were mixed in a weight ratio of 20 : 1 under agar mortar for 15 minutes, and the mixture was packed on the glass filter.

The reactants were flowed and TPR was performed from 100 °C to 700 °C with a ramp rate of 1 °C/min. The peak-shape profile of CO$_2$ was obtained and the symptom of other reactions was not detected at all in the inside and outside of the temperature range for CO$_2$ peak. The product flow was analyzed every 10 minutes with gas chromatography (Younglin, M600D). A thermal conductivity detector at 80 °C was used to quantify the gaseous products. Two on-line sampling loops and packed columns were used for separating CO$_2$ and N$_2$, respectively, from the sampled products. An MS-5A (Supelco, 1/8" O.D.×2 m, 25 °C) column was used to separate N$_2$, and CO$_2$ was separated using a Porapak-Q (Supelco 1/8" O.D.× 2 m, 50 °C) column. The carbon balance of each reaction was determined by dividing the total moles of generated CO$_2$ (obtained by integrating the molar rate of CO$_2$ over TPR run) by initial moles of carbon in the soot before reaction.

The ignition temperature of soot is determined to be the temperature when the soot combustion begins or when carbon oxides was

firstly detected. However, the determination is majorly influenced by the method to measure the concentration of CO_2. The lower limit of TCD for detecting gaseous species is generally considered to be 100 ppm. Through some inspections of our TCD system, it is concluded that the detector showed the best precision on measurement of CO_2 when the concentration was over 500 ppm. Therefore, the ignition temperature (T_{ig}) of soot was determined when 500 ppm of CO_2 was observed during a TPR run.

RESULTS AND DISCUSSION

The general TPR results are presented in Fig. 2. The detection of CO_2 preceded that of N_2, but both products disappeared simulta-

neously at the same temperature, indicating that soot acted successfully as a reductant for the NO_2 reduction. The disappearance of the N_2 signal does not mean that the window of the NOx reduc-

Table 2. Catalytic performance of several metal ion-exchanged ZSM5 catalysts for SCR of NO and NO_2 by soot. Gas composition: NO (NO_2) 1,760 ppm, O_2 5%, He balance, flow rate: 60 ml/min, amount of catalyst and soot 0.33 gram, catalyst : soot=20 : 1

Reaction 1: NO-Soot-O_2

Catalyst	Max. conversion of NO into N_2 (%)	V[N_2][a] (10^{-5} mol)	T_{ig}[b] (°C)	Carbon balance (%)
Pt-ZSM5-53	18	3.3	278	95
Cu-ZSM5-52	21	3.4	291	94
Co-ZSM5-60	19	3.7	324	98

Reaction 2: NO_2-Soot-O_2

Catalyst	Max. conversion of NO_2 into N_2 (%)	V[N_2][a] (10^{-5} mol)	T_{ig}[b] (°C)	Carbon balance (%)
Pt-ZSM5-53	19	3.8	257	100
Cu-ZSM5-52	18	4.2	286	95
Co-ZSM5-60	17	4.5	286	100

[a]Total amount of nitrogen formed throughout the TPR run
[b]Ignition temperature of soot

Table 3. Catalytic performance of several perovskite-type oxides for SCR of NO (NO_2) by soot. Gas composition: NO (NO_2) 1,760 ppm, O_2 5%, He balance, flow rate: 60 ml/min, amount of catalyst and soot 0.33 gram, catalyst : soot=20 : 1

Reaction 1: NO-Soot-O_2

Catalyst	Max. conversion of NO into N_2 (%)	V[N_2] (10^{-5} mol)	T_{ig}[b] (°C)	Carbon balance (%)
$La_{0.9}K_{0.1}CoO_3$	17	1.5	292	100
$La_{0.9}K_{0.1}MnO_3$	20	2.0	276	100
$La_{0.9}K_{0.1}Mn_{0.8}Cu_{0.2}O_3$	35	3.9	288	93
$La_{0.9}K_{0.1}FeO_3$	68	10.2	265	94
$La_{0.9}Cs_{0.1}FeO_3$	39	4.0	257	99
$La_{0.9}K_{0.1}Cu_{0.7}V_{0.3}O_x$	53	5.9	306	97
$La_{0.9}Cs_{0.1}Cu_{0.7}V_{0.3}O_x$	32	2.4	294	97
$La_{0.9}K_{0.1}VO_3$	37	2.7	331	97

Reaction 2: NO_2-Soot-O_2

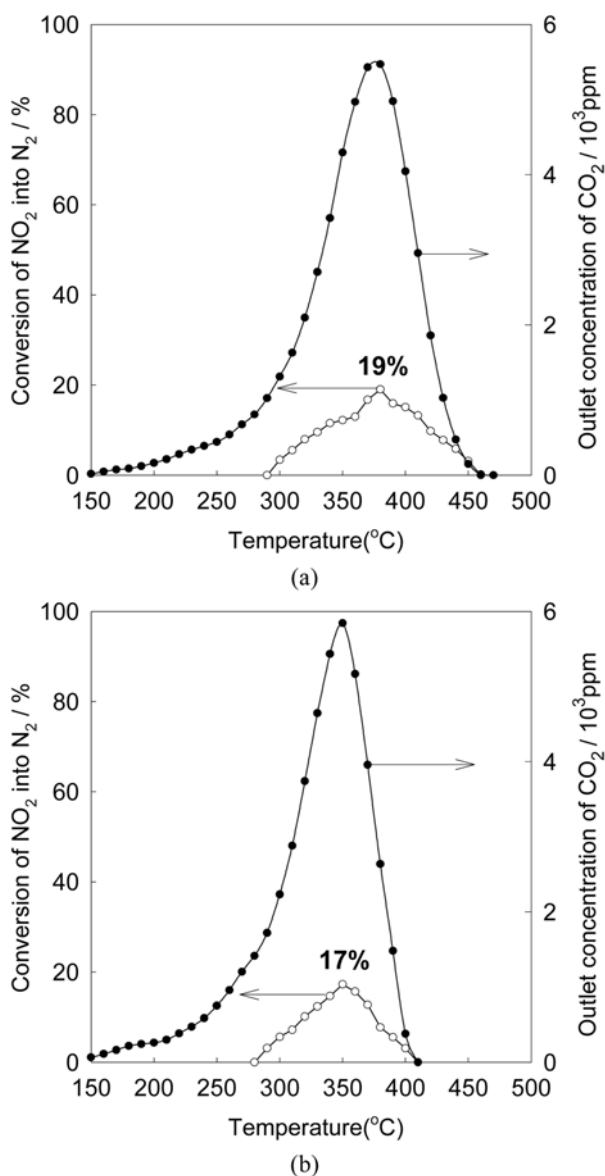| Catalyst	Max. conversion of NO_2 into N_2 (%)	V[N_2][a] (10^{-5} mol)	T_{ig}[b] (°C)	Carbon balance (%)
$La_{0.9}K_{0.1}CoO_3$	10	1.4	244	96
$La_{0.9}K_{0.1}MnO_3$	6	0.5	284	92
$La_{0.9}K_{0.1}Mn_{0.8}Cu_{0.2}O_3$	24	1.9	290	93
$La_{0.9}K_{0.1}FeO_3$	32	5.6	264	95
$La_{0.9}Cs_{0.1}FeO_3$	25	3.3	250	100
$La_{0.9}K_{0.1}Cu_{0.7}V_{0.3}O_x$	25	3.1	263	96
$La_{0.9}Cs_{0.1}Cu_{0.7}V_{0.3}O_x$	25	2.3	260	100
$La_{0.9}K_{0.1}VO_3$	23	2.6	245	96

Fig. 2. Temperature-programmed reaction (TPR) results of the simultaneous removal of NO_2 and soot over Pt-ZSM5-53. Gas composition: O_2 content (a) 5%, (b) 10%, NO_2 1,760 ppm, He balance, flow rate: 60 ml/min, amount of catalyst and soot: 0.33 gram, catalyst : soot=20 : 1.

tion activity was limited at this temperature, but rather that the reductant (soot) was completely exhausted. In addition, all the carbon balances for the tests performed in Figs. 2 and 4-6 were over 92% (Tables 2 and 3). As only CO_2 was counted in the carbon balances, it can be concluded that most of the carbon was combusted into CO_2 rather than CO.

1. Reactions between Soot and NO₂ over ZSM5 Catalysts

Table 2 presents the reaction results over Pt-, Cu- and Co-exchanged ZSM5 catalysts. Reactions were performed with NO and NO_2 and all the other reaction conditions were identical. One thing worthy of comment is that the conversion of NO to NO_2 could possibly be progressed on Pt-ZSM5, which has a possibility to have an effect on the NO reaction.

In the NOx reduction, the three ZSM5 catalysts showed similar results for both NO and NO_2. Total N_2 productions ($V[N_2]$) from the NO_2 reactions were larger than those from the NO reactions, but the maximum value in the conversion of NOx into N_2 did not change significantly. In the soot combustion, however, there were notable differences between the NO and NO_2 reactions. When NO was replaced by NO_2, the Pt and Co-ZSM5 catalysts decreased the ignition temperature of carbon by 21 and 38 °C, respectively. However, the decrease was relatively small with the Cu catalyst. As is seen in Fig. 2, by increasing the oxygen content from 5 to 10%, the total exhaustion of carbon was advanced from 460 to 410 °C, but ignition temperature remained at around 260 °C and the NOx reduction behavior was almost unaffected. Considering that the O_2 concentration was 10^5-fold greater than the NO_2 concentration, we could conclude that the oxygen exerted a very small effect on the rates of NO_2 reduction and soot combustion.

To summarize the results of the ZSM5 catalysts, Pt-ZSM5-53 showed the best performance in soot combustion and the lowest ignition temperature of 257 °C in the NO_2 reactions.

2. Reactions of Soot and NO₂ over Perovskite Catalysts

The results over the perovskite catalysts are listed in Table 3. The results from the NO_2 reaction were compared with those from the NO reaction. For the NO reactions, the catalysts $La_{0.9}K_{0.1}MnO_3$ and $La_{0.9}K_{0.1}Cu_{0.7}V_{0.3}O_x$ showed distinguished activities. The simultaneous
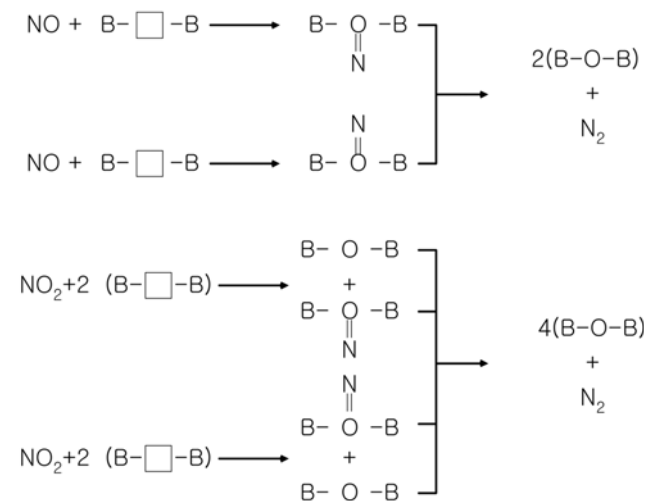

Fig. 3. Comparison of the catalytic reduction scheme of NO and NO₂ on the oxygen vacancies.

reduction of NOx and soot was reported to depend on the number and thermodynamic stability of oxygen vacancies in the perovskite catalyst [34,35]. The corresponding studies utilized NO as a NOx source, but the reaction patterns differed due to the change of NOx from NO to NO_2 in this study. First, the ignition temperatures were generally shifted to the lower region, which was similar to the previous results over the ZSM5 catalysts. This improvement was attributed to the higher combustion rate of soot when NO_2 was utilized, especially at temperatures lower than 500 °C [36-38]. However, the NOx reduction activities ($V[N_2]$ in Table 3) were depressed by the use of NO_2. According to the reports that NOx species are captured by oxygen vacancies in perovskite catalysts [39,40], the depressed activities can be explained by Fig. 3. To produce one mole of N_2
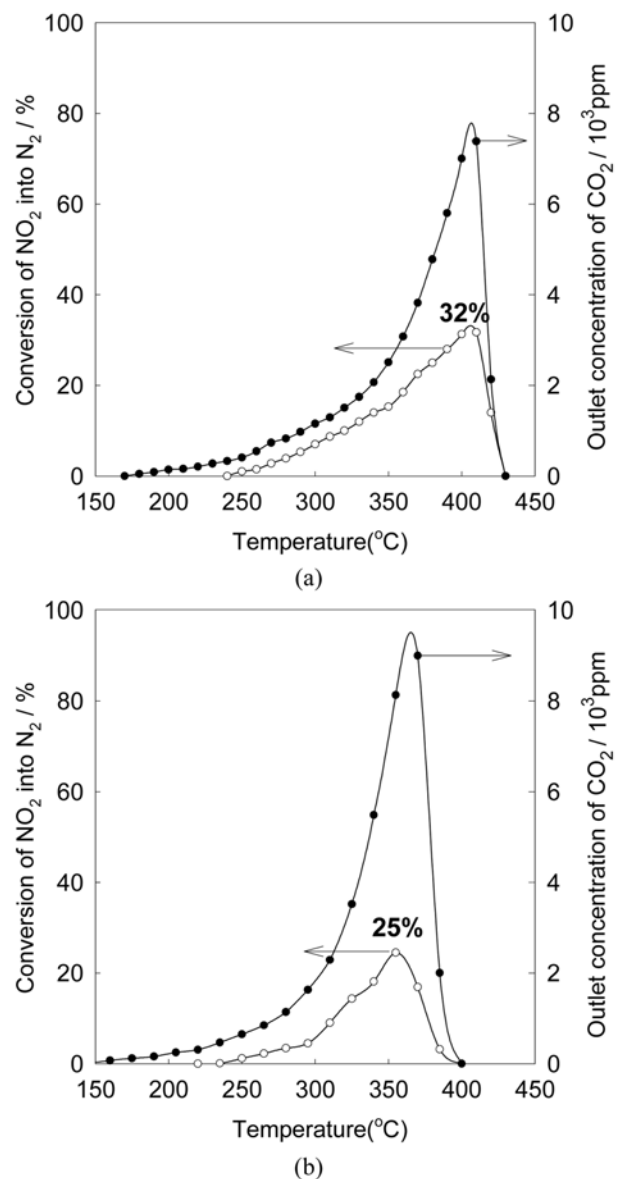

(a)

(b)

Fig. 4. Temperature-programmed reaction (TPR) results of the simultaneous removal of NO₂ and soot over La₀.₉K₀.₁FeO₃. Gas composition: O₂ content (a) 5% (b) 10%, NO₂ 1,760 ppm, He balance, flow rate: 60 ml/min, amount of catalyst and soot: 0.33 gram, catalyst : soot=20 : 1.

from NO, two moles of oxygen vacancies are needed. However, to capture NO_2, four moles of oxygen vacancies are required to produce one mole of N_2, since the dissociation of NO_2 should be preceded if it is to be captured on the vacancies, as shown in the figure. For all the perovskite catalysts listed in Table 3, the values of $V[N_2]$ were depressed when NO was replaced by NO_2, which was attributed to the requirement for more oxygen vacancies for chemisorbing NO_2 than for NO.

The activity exhibited further dependence on the concentration of oxygen vacancies again in Fig. 4, in which reaction tests were performed by changing the O_2 concentration. By increasing the O_2 content from 5 to 10%, the reduction activities of $La_{0.9}K_{0.1}FeO_3$ were notably depressed, in direct contrast to the previous cases of the ZSM5

catalysts. This result revealed that oxygen occupies the vacancies of the catalysts in competition with the NOx species.

At the rich O_2 content of 10%, the reduction activity was not improved by replacing NO_2 with NO, as shown in Figs. 4(b) and 5(b), indicating that O_2 occupied the vacancy sites of the perovskite catalysts faster than NO and NO_2. The effects of O_2 on the catalytic activities were more prominent in the NO reactions than in the NO_2 reactions. A comparison of (a) and (b) in Fig. 5 revealed that the maximum NO conversion was deceased by as much as 40%.

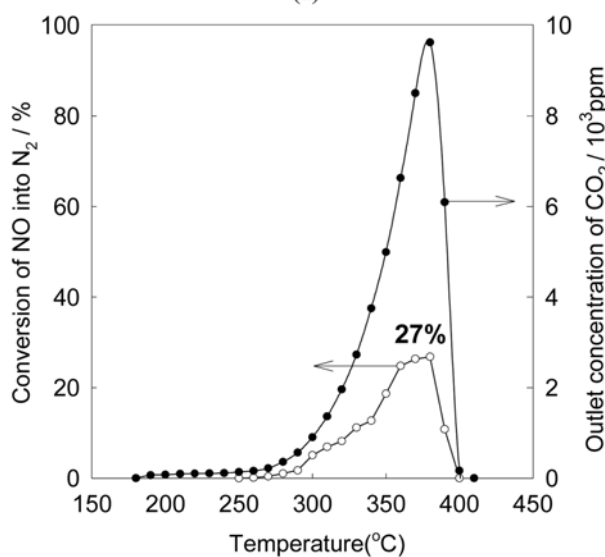**3. Reactions of Soot and NO_2 over γ-Alumina Catalyst**

The results for the NO and NO_2 reactions over γ-alumina catalyst are presented in Figs. 6(a) and (b), respectively. In contrast to the results of the ZSM5 and perovskite catalysts, the soot combustion
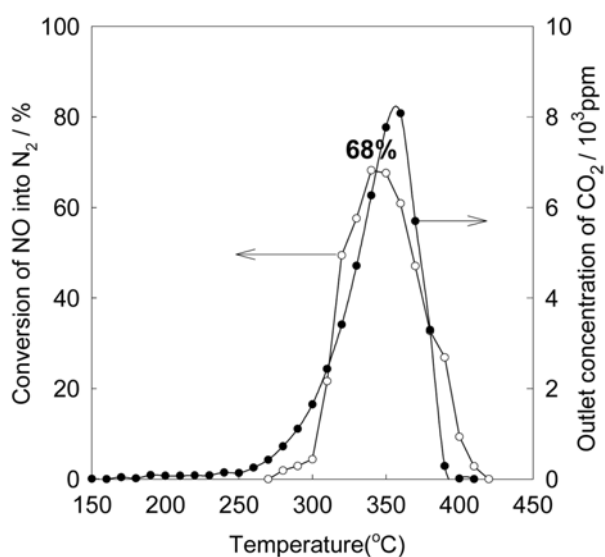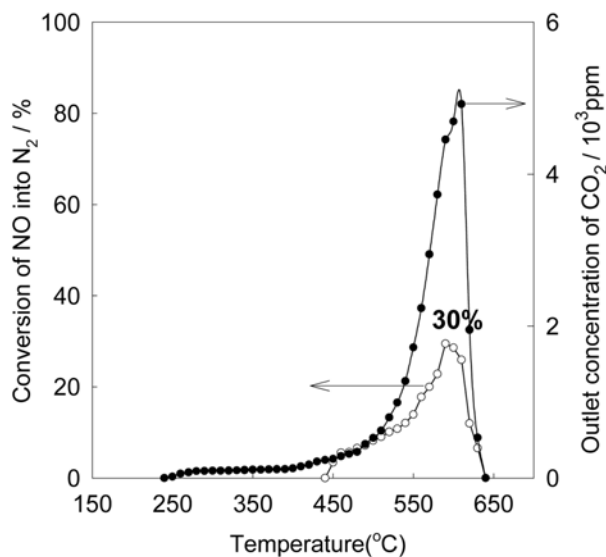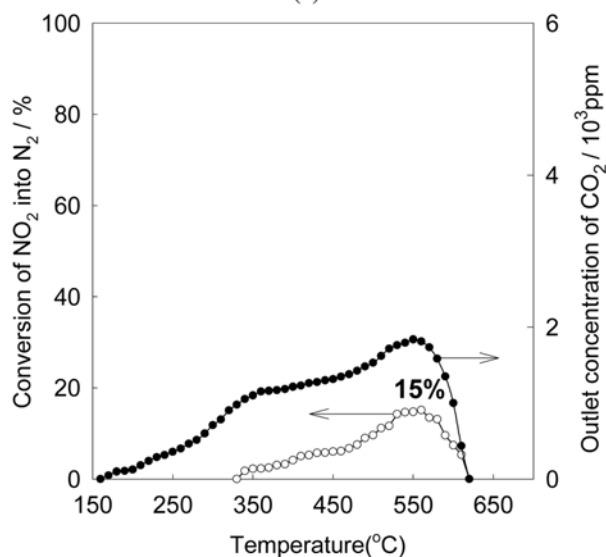

Fig. 5. Temperature-programmed reaction (TPR) results of the simultaneous removal of NO and soot over $La_{0.9}K_{0.1}FeO_3$. Gas composition: O_2 content (a) 5% (b) 10%, NO 1,760 ppm, He balance, flow rate: 60 ml/min, amount of catalyst and soot: 0.33 gram, catalyst : soot=20 : 1.

Fig. 6. Temperature-programmed reaction (TPR) results of the simultaneous removal of NO and soot over γ-alumina. Gas composition: O_2 content (a) 5% (b) 10%, NO 1,760 ppm, He balance, flow rate: 60 ml/min, amount of catalyst and soot: 0.33 gram, catalyst : soot=20 : 1.

over γ-alumina progressed at upshifted temperatures. The deNOx activities were between those of perovskite and ZSM5. The activities in the NO and NO₂ reactions differed markedly from each other. The soot combustion by NO and O_2 mostly progressed at 500-600 °C, but in the case of NO_2 and O_2, the soot was combusted at a wider temperature range of 300-550 °C. Similarly, the initiation temperature of the deNOx activity was also lowered by 100 °C (440 °C→ 340 °C) and the activity window was widened. However, the total N_2 production from the NO_2 reaction ($4.9×10^{-5}$ mol) was somewhat smaller than that from the NO reaction ($5.7×10^{-5}$ mol). Centi et al. reported that nitrite (NO_2^-) and nitrate (NO_3^-) ions were adsorbed onto the surface when γ-alumina was exposed to NO and O_2 [41]. When NO_2 was used instead, it was reported that nitrate
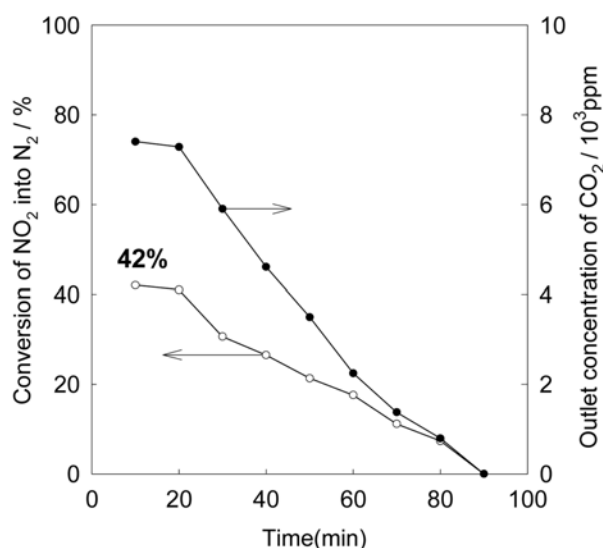
Fig. 8. Selective catalytic reduction (SCR) of NO₂ and soot over γ-Al₂O₃. Reaction temperature: 550 °C, gas composition: NO₂ 1,760 ppm, O₂ 10%, He balance, flow rate: 60 ml/min, amount of catalyst and soot: 0.33 gram, catalyst : soot=20 : 1.

ions were adsorbed onto the alumina surface more readily than other nitrite species. It was expected that soot was combusted when these NOx species were reduced to N_2, and a stronger oxidizer like nitrate ion stimulated the combustion by NO_2 and O_2 to start at a lower temperature (~150 °C) than by $NO-O_2$ (~250 °C), as displayed in Fig. 6. The low-temperature combustion afforded by NO_2 and O_2 exhausted the soot more quickly and induced the lack of reductant (soot) at the high temperature region (over 550 °C). This earlier exhaustion of soot depressed the NOx conversion in the high temperature region, thereby reducing the N_2 production compared to the $NO-O_2$ case, as in the aforementioned result.

Therefore, in order to compare the high temperature activities of NO and NO_2 reaction precisely, the reactions were performed at 550 °C isothermally, and the results are displayed in Fig. 7. In both reactions, the production of CO_2 and N_2 decreased over time, but the NO_2 reduction activity was better and the initial soot combustion rate was higher than the NO activity.

When the O_2 content was increased to 10% in the NO_2 reactions (Fig. 8), the time consumed for total soot exhaustion temperature was advanced from 180 min to 90 min and the initial NO_2 conversion to N_2 increased from 37 to 42%, which was attributed to the increase of nitrate ions with increasing oxygen content.

CONCLUSIONS

The catalytic performances of metal-exchanged ZSM5, perovskite and γ-alumina catalysts for the reduction of NO_2 by diesel soot were studied. The NO_2 was reduced to N_2 by the model soot for all the catalysts, and most of the soot was converted into CO_2. The reduction was terminated when the soot was totally exhausted, which clarified the action of the model soot as a NO_2 reductant. Pt-, Cu- and Co-exchanged ZSM5 catalysts showed similar reduction activities, with NO_2 conversions into N_2 of about 20%. The catalysts also showed similar reduction activities when NO_2 replaced NO. The
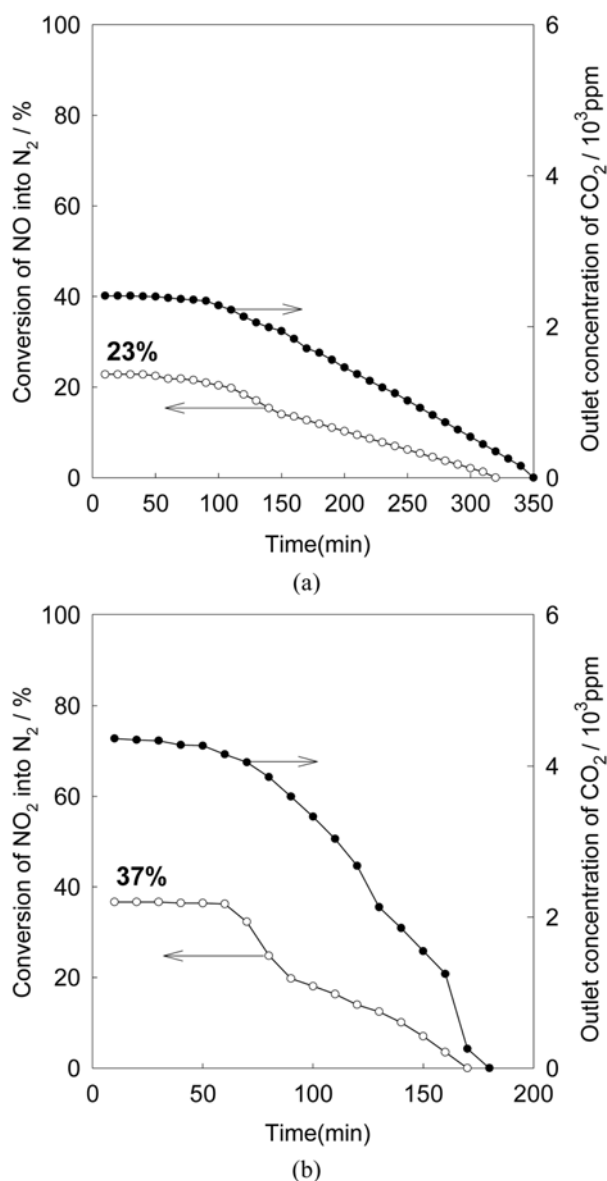

Fig. 7. Selective catalytic reduction (SCR) of NOx and soot over γ-Al₂O₃. (a) NO reaction, (b) NO₂ reaction. Reaction temperature: 550 °C, gas composition: NO (NO₂) 1,760 ppm, O₂ 5%, He balance, flow rate: 60 ml/min, amount of catalyst and soot: 0.33 gram, catalyst : soot=20 : 1.

effect of increasing O_2 content (from 5 to 10%) on the NO_2-soot reaction was relatively small for the ZSM5 catalysts. The catalytic activities of the lanthanum-based perovskite catalysts for the NO_2 reduction were lower than those when NO was used, which was attributed to the lack of available oxygen vacancies to chemisorb NO_2. The reduction activities were also depressed when the O_2 content was increased (from 5 to 10%) as the oxygen vacancies were taken up with oxygen atoms. Among the tested catalysts, $La_{0.9}K_{0.1}FeO_3$ presented the best catalytic activity in the reduction of NO_2 with a 32% conversion of NO_2 into N_2.

For the γ-alumina catalyst, the peak reduction activities occurred at a relatively high temperature around 500 °C. The catalytic performance of the γ-alumina catalyst was markedly changed when NO was replaced by NO_2. With NO_2, the soot combustion progressed at a wider and lower temperature region (300-550 °C) and the NO_2 reduction was terminated faster than for NO. The isothermal reaction tests at fixed temperature confirmed the more efficient NO_2 reduction with soot on γ-alumina compared to NO. This improved reduction activity was attributed to the formation of strong oxidant species like nitrate ions (NO_3^-) on the catalyst surface.

ACKNOWLEDGMENTS

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