

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 (NO₂) by diesel soot were investigated. The reaction tests were performed through temperature-programmed reaction (TPR), in which NO₂ and O₂ were passed through a fixed bed of catalyst-soot mixture. On the three types of catalyst, NO₂ was reduced to N₂ by model soot (Printex-U) and most of the soot was converted into CO₂. Pt-, Cu- and Co-exchanged ZSM5 catalysts exhibited reduction activities with conversions of NO₂ into N₂ of about 20%. Among the perovskite catalysts tested, La_{0.9}K_{0.1}FeO₃ showed a 32% conversion of NO₂ into N₂. 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 NO₂ 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 NO₂ from NO in diesel emissions, since NO₂ is very efficient in oxidizing carbon via the following two paths [2,5]:



Of these, route (1) is more desirable than (2) because it not only combusts solid carbons but also reduces NO_x into N₂, both of which are important for diesel exhaust aftertreatment.

Besides this on-site NO₂ production, NO₂ 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 NO₂ 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 NO₂. 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-O₂ environment, while very few studies have dealt with the soot combustion under a NO₂-O₂ environment [9,10].

About a decade ago, diesel soot was not generally accepted as a candidate for NO_x reductant. However, Teraoka and colleagues have reported several studies [11-13] on NO_x reduction with soot materials, which revealed that diesel soot could be used as a reductant for lean deNO_x, especially in the presence of perovskite and spinel-type catalysts. (Perovskite catalyst is also known to remove NO_x with hydrocarbon [14].) Because diesel soot contains 2.2 wt% of hydrogen on average, NO_x 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-O₂ 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-O₂ 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-O₂ environment [27-30].

γ -Alumina was reported to show high deNO_x performance when NO₂ was fed as the NO_x species [31,32]. This performance was also confirmed in a study about plasma-enhanced catalysis [33], where plasma was used to convert NO into NO₂ and alumina effectively reduced this NO₂ with hydrocarbons.

In this study, we investigated and compared the performances of lean NO₂ reduction with diesel soot under ZSM5, perovskite and γ -alumina catalysts. We checked the concentrations of N₂ and CO₂

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*This paper is dedicated to Professor Jae Chun Hyun for celebrating his retirement from Department of Chemical and Biological Engineering of Korea University.

for every reaction to determine the effectiveness of each catalyst's activity in promoting the reaction route (1). Soot-NO-O₂ reactions were also tested over the catalysts and the results were used to clarify the characteristics of the soot-NO₂-O₂ 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 SiO₂/Al₂O₃=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 m²/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 μ m. Because the average diameter of diesel soot is known to range from 0.01 to 2.5 μ m, 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 |

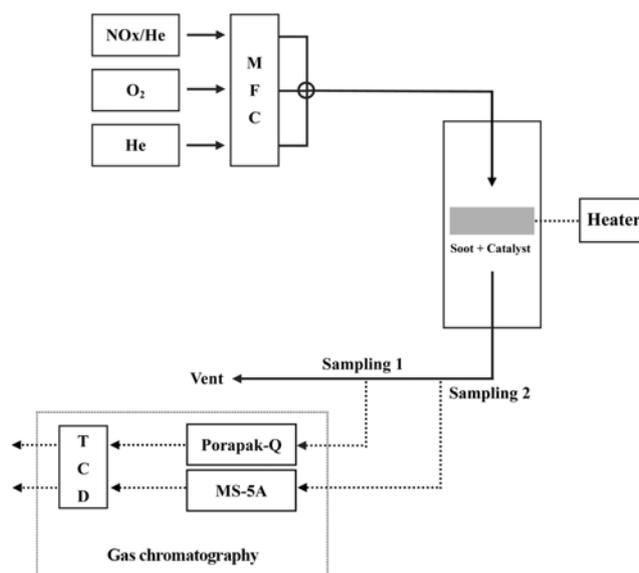


Fig. 1. Schematic of instrumental set-up for the reaction tests.

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. NO₂ (or NO) gas at 1,980 ppm in helium balance (PS Chem) was used and mixed with oxygen (PS Chem, 99.999%) and additional helium (PS Chem, 99.999%) to make a reaction gas consisting of 1,760 ppm NO₂ (or NO) and 5 (or 10) % O₂. 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 CO₂ was obtained and the symptom of other reactions was not detected at all in the inside and outside of the temperature range for CO₂ 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 CO₂ and N₂, respectively, from the sampled products. An MS-5A (Supelco, 1/8" O.D.×2 m, 25 °C) column was used to separate N₂, and CO₂ 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 CO₂ (obtained by integrating the molar rate of CO₂ 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-

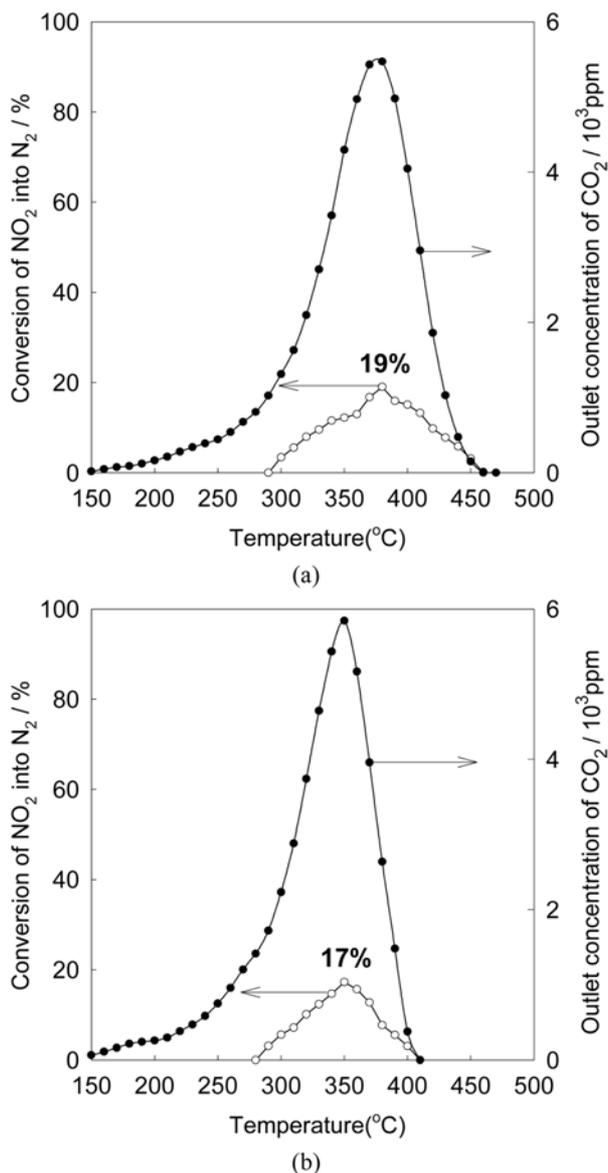


Fig. 2. Temperature-programmed reaction (TPR) results of the simultaneous removal of NO_2 and soot over Pt-ZSM5-53. Gas composition: O_2 content (a) 5%, (b) 10%, NO_2 1,760 ppm, He balance, flow rate: 60 ml/min, amount of catalyst and soot: 0.33 gram, catalyst : soot=20 : 1.

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 NO_x 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 (%) | $V[\text{N}_2]^a$ (10^{-5} mol) | T_{ig}^b ($^\circ\text{C}$) | 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 (%) | $V[\text{N}_2]^a$ (10^{-5} mol) | T_{ig}^b ($^\circ\text{C}$) | 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 |

^aTotal amount of nitrogen formed throughout the TPR run

^bIgnition 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 (%) | $V[\text{N}_2]$ (10^{-5} mol) | T_{ig}^b ($^\circ\text{C}$) | Carbon balance (%) |
| $\text{La}_{0.9}\text{K}_{0.1}\text{CoO}_3$ | 17 | 1.5 | 292 | 100 |
| $\text{La}_{0.9}\text{K}_{0.1}\text{MnO}_3$ | 20 | 2.0 | 276 | 100 |
| $\text{La}_{0.9}\text{K}_{0.1}\text{Mn}_{0.8}\text{Cu}_{0.2}\text{O}_3$ | 35 | 3.9 | 288 | 93 |
| $\text{La}_{0.9}\text{K}_{0.1}\text{FeO}_3$ | 68 | 10.2 | 265 | 94 |
| $\text{La}_{0.9}\text{Cs}_{0.1}\text{FeO}_3$ | 39 | 4.0 | 257 | 99 |
| $\text{La}_{0.9}\text{K}_{0.1}\text{Cu}_{0.7}\text{V}_{0.3}\text{O}_x$ | 53 | 5.9 | 306 | 97 |
| $\text{La}_{0.9}\text{Cs}_{0.1}\text{Cu}_{0.7}\text{V}_{0.3}\text{O}_x$ | 32 | 2.4 | 294 | 97 |
| $\text{La}_{0.9}\text{K}_{0.1}\text{VO}_3$ | 37 | 2.7 | 331 | 97 |
| Reaction 2: NO_2 -Soot- O_2 | | | | |
| Catalyst | Max. conversion of NO_2 into N_2 (%) | $V[\text{N}_2]^a$ (10^{-5} mol) | T_{ig}^b ($^\circ\text{C}$) | Carbon balance (%) |
| $\text{La}_{0.9}\text{K}_{0.1}\text{CoO}_3$ | 10 | 1.4 | 244 | 96 |
| $\text{La}_{0.9}\text{K}_{0.1}\text{MnO}_3$ | 6 | 0.5 | 284 | 92 |
| $\text{La}_{0.9}\text{K}_{0.1}\text{Mn}_{0.8}\text{Cu}_{0.2}\text{O}_3$ | 24 | 1.9 | 290 | 93 |
| $\text{La}_{0.9}\text{K}_{0.1}\text{FeO}_3$ | 32 | 5.6 | 264 | 95 |
| $\text{La}_{0.9}\text{Cs}_{0.1}\text{FeO}_3$ | 25 | 3.3 | 250 | 100 |
| $\text{La}_{0.9}\text{K}_{0.1}\text{Cu}_{0.7}\text{V}_{0.3}\text{O}_x$ | 25 | 3.1 | 263 | 96 |
| $\text{La}_{0.9}\text{Cs}_{0.1}\text{Cu}_{0.7}\text{V}_{0.3}\text{O}_x$ | 25 | 2.3 | 260 | 100 |
| $\text{La}_{0.9}\text{K}_{0.1}\text{VO}_3$ | 23 | 2.6 | 245 | 96 |

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 CO₂ was counted in the carbon balances, it can be concluded that most of the carbon was combusted into CO₂ 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 NO₂ and all the other reaction conditions were identical. One thing worthy of comment is that the conversion of NO to NO₂ could possibly be progressed on Pt-ZSM5, which has a possibility to have an effect on the NO reaction.

In the NO_x reduction, the three ZSM5 catalysts showed similar results for both NO and NO₂. Total N₂ productions (V[N₂]) from the NO₂ reactions were larger than those from the NO reactions, but the maximum value in the conversion of NO_x into N₂ did not change significantly. In the soot combustion, however, there were notable differences between the NO and NO₂ reactions. When NO was replaced by NO₂, 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 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 NO_x reduction behavior was almost unaffected. Considering that the O₂ concentration was 10⁵-fold greater than the NO₂ concentration, we could conclude that the oxygen exerted a very small effect on the rates of NO₂ 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 NO₂ 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 NO₂ reaction were compared with those from the NO reaction. For the NO reactions, the catalysts La_{0.9}K_{0.1}MnO₃ and La_{0.9}K_{0.1}Cu_{0.7}V_{0.3}O_x showed distinguished activities. The simultaneous

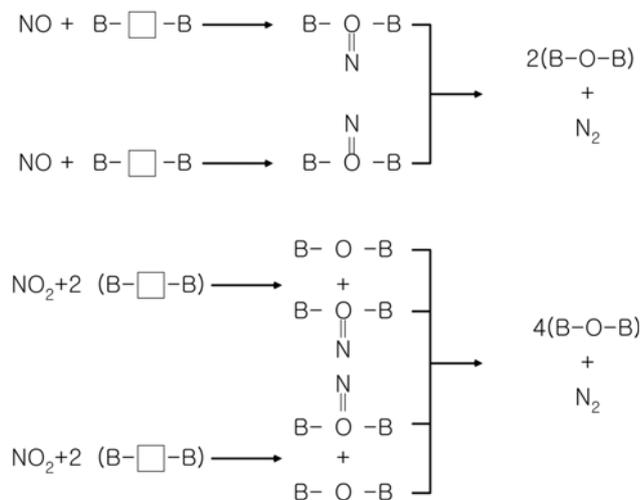


Fig. 3. Comparison of the catalytic reduction scheme of NO and NO₂ on the oxygen vacancies.

reduction of NO_x 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 NO_x source, but the reaction patterns differed due to the change of NO_x from NO to NO₂ 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 NO₂ was utilized, especially at temperatures lower than 500 °C [36-38]. However, the NO_x reduction activities (V[N₂] in Table 3) were depressed by the use of NO₂. According to the reports that NO_x 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 N₂

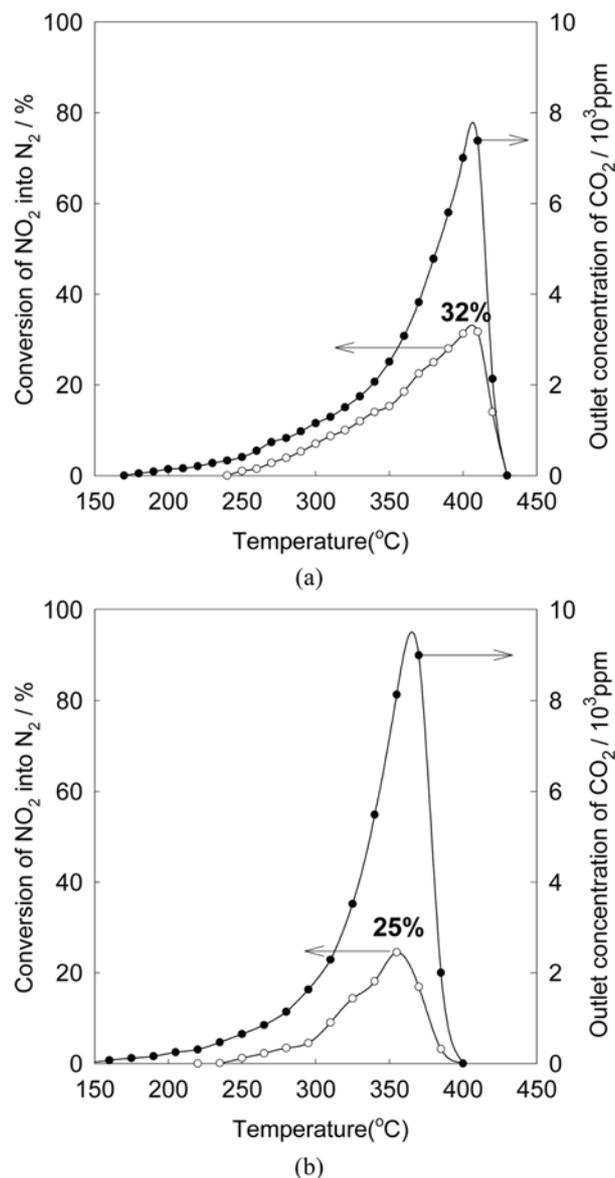


Fig. 4. Temperature-programmed reaction (TPR) results of the simultaneous removal of NO₂ and soot over La_{0.9}K_{0.1}FeO₃. Gas composition: O₂ content (a) 5% (b) 10%, NO₂ 1,760 ppm, He balance, flow rate: 60 ml/min, amount of catalyst and soot: 0.33 gram, catalyst : soot=20 : 1.

from NO, two moles of oxygen vacancies are needed. However, to capture NO₂, four moles of oxygen vacancies are required to produce one mole of N₂, since the dissociation of NO₂ 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[N₂] were depressed when NO was replaced by NO₂, which was attributed to the requirement for more oxygen vacancies for chemisorbing NO₂ than for NO.

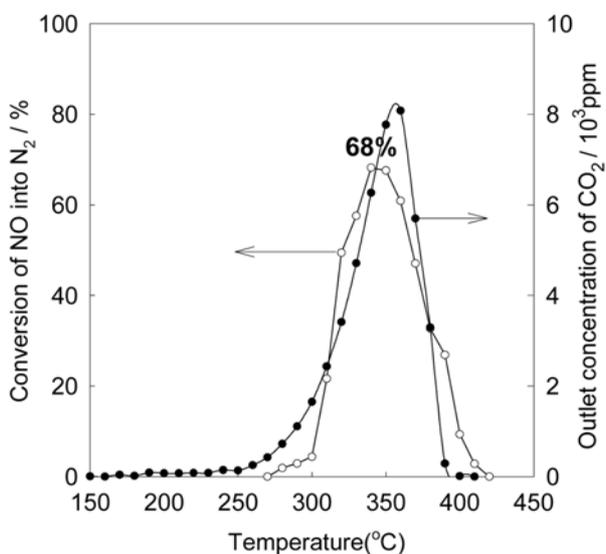
The activity exhibited further dependence on the concentration of oxygen vacancies again in Fig. 4, in which reaction tests were performed by changing the O₂ concentration. By increasing the O₂ content from 5 to 10%, the reduction activities of La_{0.9}K_{0.1}FeO₃ were notably depressed, in direct contrast to the previous cases of the ZSM5

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

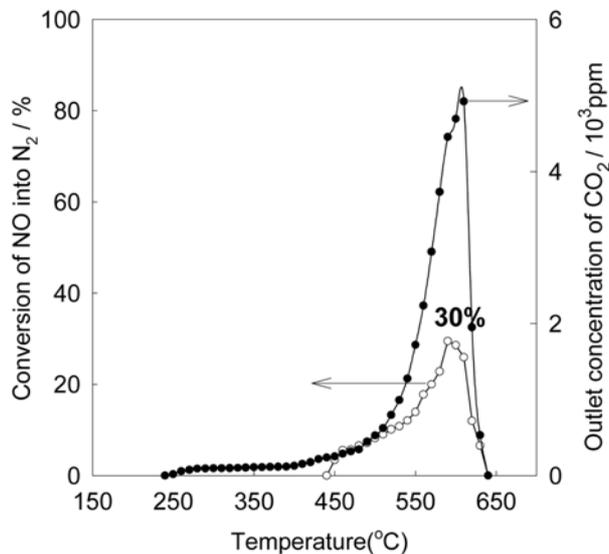
At the rich O₂ content of 10%, the reduction activity was not improved by replacing NO₂ with NO, as shown in Figs. 4(b) and 5(b), indicating that O₂ occupied the vacancy sites of the perovskite catalysts faster than NO and NO₂. The effects of O₂ on the catalytic activities were more prominent in the NO reactions than in the NO₂ reactions. A comparison of (a) and (b) in Fig. 5 revealed that the maximum NO conversion was decreased by as much as 40%.

3. Reactions of Soot and NO₂ over γ -Alumina Catalyst

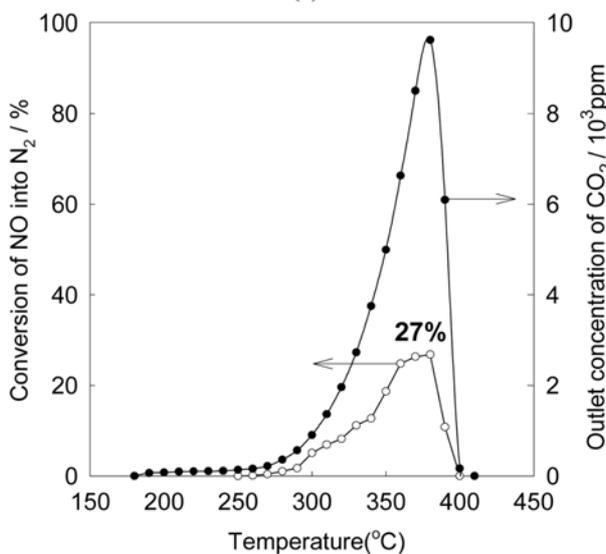
The results for the NO and NO₂ reactions over γ -alumina catalyst are presented in Figs. 6(a) and (b), respectively. In contrast to the results of the ZSM5 and perovskite catalysts, the soot combustion



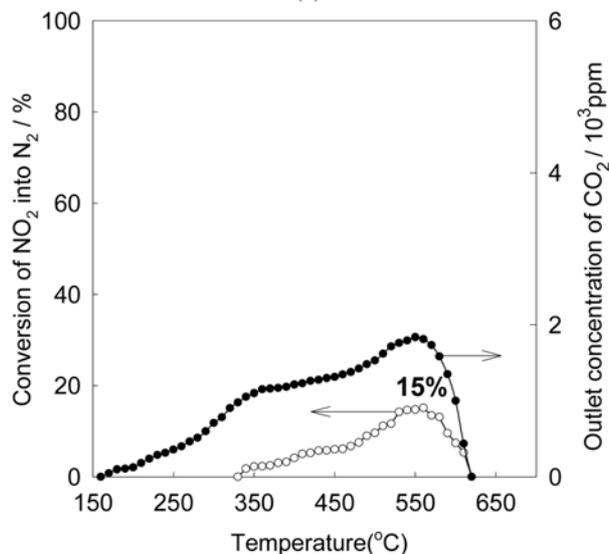
(a)



(a)



(b)



(b)

Fig. 5. Temperature-programmed reaction (TPR) results of the simultaneous removal of NO and soot over La_{0.9}K_{0.1}FeO₃. Gas composition: O₂ 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: O₂ 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 deNO_x 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 O₂ mostly progressed at 500-600 °C, but in the case of NO₂ and O₂, the soot was combusted at a wider temperature range of 300-550 °C. Similarly, the initiation temperature of the deNO_x activity was also lowered by 100 °C (440 °C → 340 °C) and the activity window was widened. However, the total N₂ production from the NO₂ 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 (NO₂⁻) and nitrate (NO₃⁻) ions were adsorbed onto the surface when γ -alumina was exposed to NO and O₂ [41]. When NO₂ was used instead, it was reported that nitrate

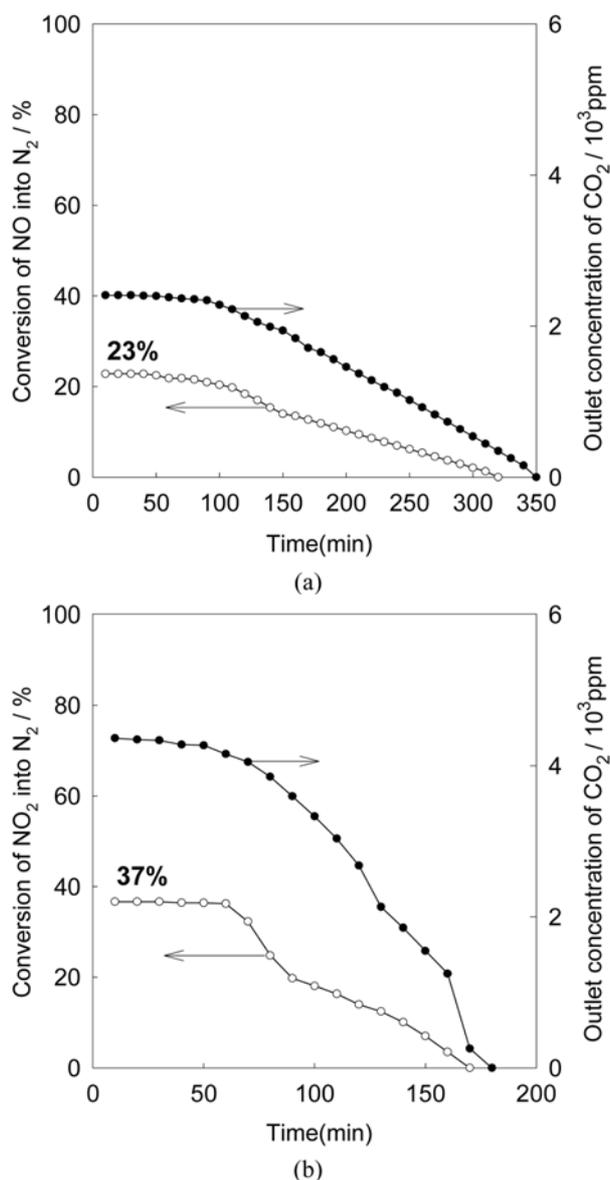


Fig. 7. Selective catalytic reduction (SCR) of NO_x and soot over γ -Al₂O₃. (a) NO reaction, (b) NO₂ reaction. Reaction temperature: 550 °C, gas composition: NO (NO₂) 1,760 ppm, O₂ 5%, He balance, flow rate: 60 ml/min, amount of catalyst and soot: 0.33 gram, catalyst : soot=20 : 1.

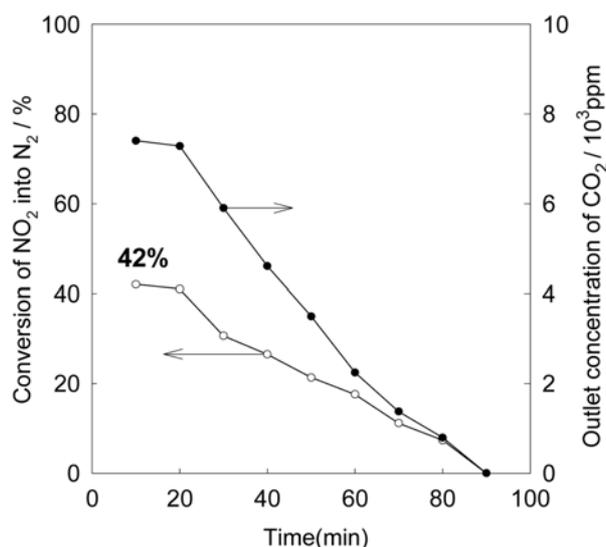


Fig. 8. Selective catalytic reduction (SCR) of NO₂ and soot over γ -Al₂O₃. Reaction temperature: 550 °C, gas composition: NO₂ 1,760 ppm, O₂ 10%, He balance, flow rate: 60 ml/min, amount of catalyst and soot: 0.33 gram, catalyst : soot=20 : 1.

ions were adsorbed onto the alumina surface more readily than other nitrite species. It was expected that soot was combusted when these NO_x species were reduced to N₂, and a stronger oxidizer like nitrate ion stimulated the combustion by NO₂ and O₂ to start at a lower temperature (~150 °C) than by NO-O₂ (~250 °C), as displayed in Fig. 6. The low-temperature combustion afforded by NO₂ and O₂ 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 NO_x conversion in the high temperature region, thereby reducing the N₂ production compared to the NO-O₂ case, as in the aforementioned result.

Therefore, in order to compare the high temperature activities of NO and NO₂ reaction precisely, the reactions were performed at 550 °C isothermally, and the results are displayed in Fig. 7. In both reactions, the production of CO₂ and N₂ decreased over time, but the NO₂ reduction activity was better and the initial soot combustion rate was higher than the NO activity.

When the O₂ content was increased to 10% in the NO₂ reactions (Fig. 8), the time consumed for total soot exhaustion temperature was advanced from 180 min to 90 min and the initial NO₂ conversion to N₂ 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 NO₂ by diesel soot were studied. The NO₂ was reduced to N₂ by the model soot for all the catalysts, and most of the soot was converted into CO₂. The reduction was terminated when the soot was totally exhausted, which clarified the action of the model soot as a NO₂ reductant. Pt-, Cu- and Co-exchanged ZSM5 catalysts showed similar reduction activities, with NO₂ conversions into N₂ of about 20%. The catalysts also showed similar reduction activities when NO₂ replaced NO. The

effect of increasing O₂ content (from 5 to 10%) on the NO₂-soot reaction was relatively small for the ZSM5 catalysts. The catalytic activities of the lanthanum-based perovskite catalysts for the NO₂ reduction were lower than those when NO was used, which was attributed to the lack of available oxygen vacancies to chemisorb NO₂. The reduction activities were also depressed when the O₂ 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}FeO₃ presented the best catalytic activity in the reduction of NO₂ with a 32% conversion of NO₂ into N₂.

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 NO₂. With NO₂, the soot combustion progressed at a wider and lower temperature region (300-550 °C) and the NO₂ reduction was terminated faster than for NO. The isothermal reaction tests at fixed temperature confirmed the more efficient NO₂ 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 (NO₃⁻) on the catalyst surface.

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