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# Simultaneous catalytic removal of nitrogen oxides and diesel soot particulate over perovskite-related oxides

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## Abstract

Catalytic performance of perovskite-type ($ABO_3$) and $K_2NiF_4$-type ($A_2BO_4$) oxides for the reduction of $NO_x$ by diesel soot particulate in the presence of excess oxygen, that is, the simultaneous removal of $NO_x$ and soot, has been investigated. Their catalytic activity, evaluated from the ignition temperature of soot and selectivity to $NO_x$ reduction into nitrogen largely depended on both *A*-site and *B*-site cations and the partial substitution of potassium at *A*-sites prominently promoted both the activity and selectivity. These mixed metal oxide catalysts were superior to transition metal simple oxides and $Pt/Al_2O_3$ in the selectivity for $NO_x$ reduction. The ignition temperature of soot in $NO + O_2$ gas stream was lower than that in NO or $O_2$ gas stream, implying that nitrogen dioxide accelerates the oxidation or activation of soot.

*Keywords*: $NO_x$; Diesel soot particulate; Perovskite-related oxides

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## 1. Introduction

Nitrogen oxides ($NO_x$) and soot particulate emitted from diesel exhaust have been causing severe environmental and health problems. Since the simultaneous reduction of $NO_x$ and particulate emissions cannot be accomplished by engine modifications alone, catalytic processes for reducing the emission of both harmful substances should be developed. As one promising process to meet this demand, Yoshida et al. [1] proposed the catalytic process by which both $NO_x$ and soot particulate 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 contact between catalyst and trapped soot. We have already reported in communication papers [2,3] that perovskite-type ($ABO_3$) and spinel-type ($AB_2O_4$) oxides showed the catalytic activity for the simultaneous removal of $NO_x$ and soot particulate.

This paper concerns with the catalytic performance of perovskite-type ($ABO_3$) and $K_2NiF_4$-type ($A_2BO_4$) oxides for the simultaneous removal of $NO_x$ and soot, that is, the reduction of $NO_x$ by soot in the presence of excess oxygen.

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## 2. Experimental

### 2.1. Catalyst preparation

Mixed metal oxide catalysts were synthesized from nitrates (Fe and Cs), $NH_4VO_3$ and acetates (others) by calcining at 850°C for 10 h in air. The formation of perovskite-type and $K_2NiF_4$-type (K-type) oxides was confirmed by X-ray diffraction using Cu K$\alpha$ radiation. Substitution levels ($x$) of strontium for lanthanum in perovskite-type oxides were set at those reported to give the highest oxidation activity in each system [4]; $x = 0.6$ for Mn-containing oxides and $x = 0.2$ for oxides with a single *B*-site cation of cobalt or iron. On the other hand, the substitution level of potassium was set at 0.1 for perovskites or less than 0.15 for K-type oxides in consideration of differences in ionic size and valency between lanthanum and potassium. 0.5 wt.-% Pt/$Al_2O_3$ (N.E. Chemcat.) and transition metal oxides ($MnO_2$, $Fe_2O_3$, CuO, $V_2O_5$) were commercially obtained and used as received and $Co_3O_4$ was prepared by the decomposition of cobalt(II)acetate at 600°C for 5 h in air.

### 2.2. Reaction study

The diesel soot particulate was obtained by the incomplete combustion of diesel fuel and the soluble organic fraction was less than 5% in weight. The catalyst and the soot (ca. 5 wt.-%) were well mixed in an agate mortar with a pestle for more than 10 min. Although the soot/catalyst contact is known to significantly affect the results [5], this mixing procedure gave reproducible results under the present experimental conditions. The catalyst/soot mixture (0.33 g) was placed in a quartz-tube reactor and, after the pretreatment at 400°C for 3 h and cooling down to 100°C in a He stream, the temperature programmed reaction (TPR) was started at the heating rate of 1°C $min^{-1}$ in a gaseous mixture of NO (0.5%), $O_2$ (5%) and He (balance) (flow rate; 20 $cm^3$ $min^{-1}$). TPR measurements were also performed in NO (10%) and He (balance) and $O_2$ (5%) and He (balance) gas streams. The outlet gas was analyzed by gas chromatography with intervals of about 15 min. In order to collect information about the catalytic activity of oxide catalysts for the gas-phase oxidation reaction, methane oxidation activity was measured under an isothermal condition by feeding the reaction gas, $CH_4$ (2.0 vol.-%) diluted in air, with a contact time of 1.5 g s $cm^{-3}$.

## 3. Results and discussion

### 3.1. Simultaneous removal reaction of $NO_x$ and soot particulate

Fig. 1 shows a typical result of TPR over $La_{1.9}K_{0.1}Cu_{0.95}V_{0.05}O_4$. The formation of carbon dioxide due to the oxidation of the soot and the reduction of $NO_x$ into nitrogen were observed at the same temperature range and curves of carbon dioxide and nitrogen formation were very similar in shape. This clearly indicates the occurrence of the simultaneous removal of $NO_x$ and soot. The sudden drops of carbon dioxide and nitrogen formation at higher temperatures are of course due to the exhaustion of the charged soot. Within the rising portion of carbon dioxide and nitrogen formation curves where the sufficient amount of the charged soot still remains, Arrhenius-type plots of the reaction rates give straight lines (Fig. 2), indi-

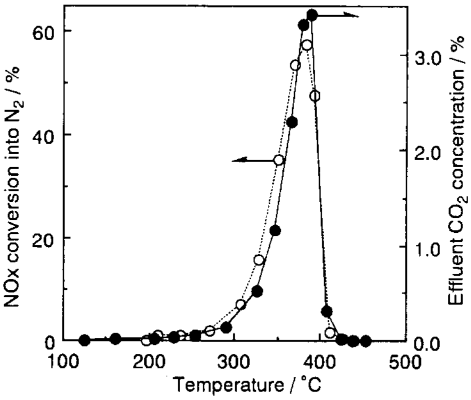

Fig. 1. Temperature programmed reaction of the simultaneous removal of $NO_x$ and diesel soot particulate over $La_{1.9}K_{0.1}Cu_{0.95}V_{0.05}O_4$.

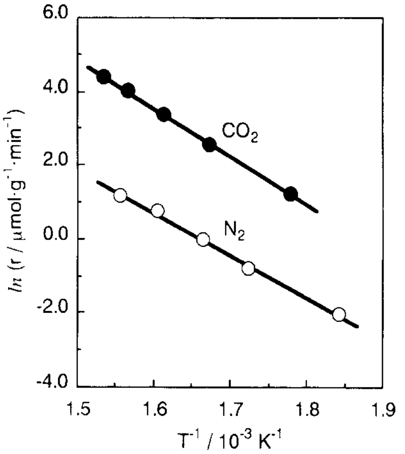

Fig. 2. Arrhenius-type plots of rates of carbon dioxide and nitrogen formation over $La_{1.9}K_{0.1}Cu_{0.95}V_{0.05}O_4$.

cating that the reaction is thermally well controlled. For all the catalysts tested, nitrogen was a sole observed product of $NO_x$ reduction and nitrous oxide was never detected. The soot was practically oxidized to carbon dioxide; a small amount of carbon monoxide, the selectivity to which ($[CO]/[CO_2] + [CO]$) was less than 5%, was detected only for $La_{0.8}K_{0.2}CoO_3$, $La_{0.8}Sr_{0.2}FeO_3$ and $La_{0.9}K_{0.1}FeO_3$. The material balance with respect to carbon was 97–102% if we assume that the soot consists of only carbon.

From TPR results, two parameters are derived in order to evaluate the catalytic performance; one is the ignition temperature of the soot ($T_{ig}$) estimated by extrapolating the steeply ascending portion of the carbon dioxide formation curve to zero carbon dioxide concentration (estimation error; ± 5°C) and the other is the total amount of nitrogen formed throughout the TPR run ($V[N_2]$) obtained by integrating the conversion into nitrogen versus temperature (time) curve. Table 1 lists values of $T_{ig}$ and $V[N_2]$ thus obtained for all the mixed metal oxide catalysts together with the

Table 1
Catalytic performance of perovskite-type and $K_2NiF_4$-type oxides synthesized in this study for the simultaneous removal of $NO_x$ and diesel soot particulate

| Catalyst | | $S_a$[a] ($m^2 g^{-1}$) | $T_{ig}$[b] (°C) | $V[N_2]$[c] ($10^{-5}$ mol) | Selectivity[d] (%) |
|---|---|---|---|---|---|
| Perovskite-type oxide | | | | | |
| 1 | $La_{0.8}Sr_{0.2}CoO_3$ | 5.6 | 270 | 2.05 | 1.5 |
| 2 | $La_{0.95}K_{0.05}CoO_3$ | 1.3 | 261 | 3.18 | 2.3 |
| 3 | $La_{0.9}K_{0.1}CoO_3$ | 0.6 | 240 | 3.39 | 2.5 |
| 4 | $La_{0.8}K_{0.2}CoO_3$ | 0.6 | 278 | 2.46 | 1.8 |
| 5 | $La_{0.9}Li_{0.1}CoO_3$ | 1.6 | 262 | 2.75 | 2.0 |
| 6 | $La_{0.9}Cs_{0.1}CoO_3$ | 0.8 | 267 | 3.87 | 2.8 |
| 7 | $La_{0.4}Sr_{0.6}MnO_3$ | 4.0 | 285 | 3.04 | 2.2 |
| 8 | $La_{0.9}K_{0.1}MnO_3$ | 2.9 | 269 | 3.83 | 2.8 |
| 9 | $La_{0.8}Sr_{0.2}FeO_3$ | 6.7 | 315 | 3.21 | 2.3 |
| 10 | $La_{0.9}K_{0.1}FeO_3$ | 3.5 | 276 | 6.95 | 5.1 |
| 11 | $La_{0.4}Sr_{0.6}Mn_{0.8}Fe_{0.2}O_3$ | 11.5 | 270 | 2.66 | 1.9 |
| 12 | $La_{0.9}K_{0.1}Mn_{0.8}Fe_{0.2}O_3$ | 5.6 | 258 | 4.95 | 3.6 |
| 13 | $La_{0.4}Sr_{0.6}Mn_{0.8}Cu_{0.2}O_3$ | 5.7 | 285 | 4.64 | 3.4 |
| 14 | $La_{0.9}K_{0.1}Mn_{0.8}Cu_{0.2}O_3$ | 2.4 | 270 | 6.20 | 4.5 |
| $K_2NiF_4$-type oxide | | | | | |
| 15 | $La_2CuO_4$ | 1.3 | 317 | 4.80 | 3.5 |
| 16 | $La_2Cu_{0.95}V_{0.05}O_4$ | 3.3 | 321 | 4.60 | 3.3 |
| 17 | $La_{1.94}Sr_{0.06}Cu_{0.95}V_{0.05}O_4$ | 4.7 | 295 | 5.30 | 3.9 |
| 18 | $La_{1.97}K_{0.03}Cu_{0.95}V_{0.05}O_4$ | 2.8 | 310 | 5.35 | 3.9 |
| 19 | $La_{1.95}K_{0.05}Cu_{0.95}V_{0.05}O_4$ | 2.2 | 300 | 7.80 | 5.7 |
| 20 | $La_{1.9}K_{0.1}Cu_{0.95}V_{0.05}O_4$ | 1.6 | 295 | 8.05 | 5.9 |
| 21 | $La_{1.85}K_{0.15}Cu_{0.95}V_{0.05}O_4$ | 1.4 | 294 | 5.72 | 4.2 |

[a] Specific surface area.
[b] Ignition temperature of soot (see text).
[c] Total amount of nitrogen formed throughout the TPR run (see text).
[d] Selectivity to $NO_x$ reduction (see text).

selectivity to $NO_x$ reduction defined as the molar ratio of the formed nitrogen to the charged soot assumed to be carbon. This definition of the selectivity which is based on the reaction $C+(2-2x)NO+xO_2 \rightarrow CO_2+(1-x)N_2$ is reasonable because the carbon balance was quite good under the assumption that the soot consists of only carbon and the amount of CO, if formed, was quite low. Note that the selectivity to $NO_x$ reduction is only 5.9% for the most selective $La_{1.9}K_{0.1}Cu_{0.95}V_{0.05}O_4$ and therefore the oxidation of the soot by oxygen predominates over that by $NO_x$ in the present reaction system.

In order to examine the effect of the soot to catalyst ratio, TPR experiment was carried out with 12 wt.-% soot/$La_{0.9}K_{0.1}CoO_3$ mixture. Total amount of carbon dioxide and nitrogen formed increased as compared with the 5 wt.-% mixture, but the selectivity to $NO_x$ reduction (2.3%) was almost the same as that observed with the 5 wt.-% mixture (2.5%). Furthermore, $T_{ig}$ were close to each other, 240°C (5 wt.-%) and 245°C (12 wt.-%), though temperatures for maxima and completion of carbon dioxide and nitrogen formation were higher by about 30°C in the case of the 12 wt.-% mixture. These results clearly indicates that the soot to catalyst ratio little influence the catalytic performance of the simultaneous $NO_x$ and soot removal under the present experimental conditions.

### 3.2. *Effect of oxide composition*

Fig. 3 shows the relation between $V[N_2]$ and $T_{ig}$ of the representative catalysts. Naturally a good catalyst with high activity and selectivity should be the oxide with low $T_{ig}$ and large $V[N_2]$. It can be seen that the selectivity to $NO_x$ reduction of $Pt/Al_2O_3$ and simple transition metal oxides are low except for $Fe_2O_3$ and that perovskite-related oxides are superior to simple oxides with respect to the selectivity to $NO_x$ reduction.

The catalytic performance of perovskite-related oxides changed significantly depending on 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 performance.

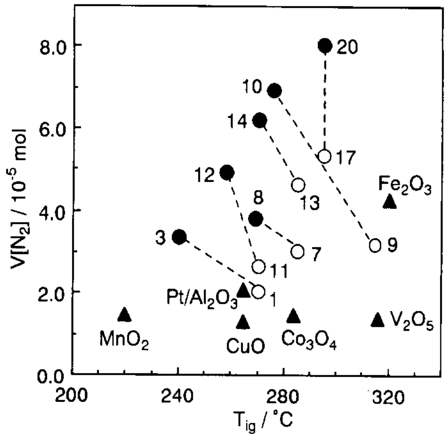

Fig. 3. Relation between the amount of nitrogen formed throughout the TPR run ($V[N_2]$) and the ignition temperature of soot ($T_{ig}$). See Table 1 for the listing of catalysts. Broken lines show a pair of Sr-substituted (open circle) and K-substituted (closed circle) oxides with the same *B*-site cation(s).

#### *Effect of B-site cations*

In either series of K- or Sr-substituted oxides, the trade-off relation that $V[N_2]$ tends to decrease with decreasing $T_{ig}$ is observed. 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 [4] and judging from $T_{ig}$, this activity order with respect to the *B*-site cations is also true in the present $NO_x$-$O_2$-soot reaction. These results may indicate that it is difficult to promote the catalytic performance for the simultaneous removal of $NO_x$ and soot solely by the change of *B*-site composition.

#### *Effect of A-site cations*

By changing the *A*-site substitute from strontium to potassium, the prominent promotion effect with increasing $V[N_2]$ and decreasing $T_{ig}$ was observed. In each pair of the catalysts with the same *B*-site cation(s) which are connected with a broken line in Fig. 3, K-substituted oxides showed higher $V[N_2]$ and lower $T_{ig}$ than Sr-substituted oxides. As seen from the results on Co-based perovskite-type oxides (Table 1), the promotion effect was also observed with other alkaline met-

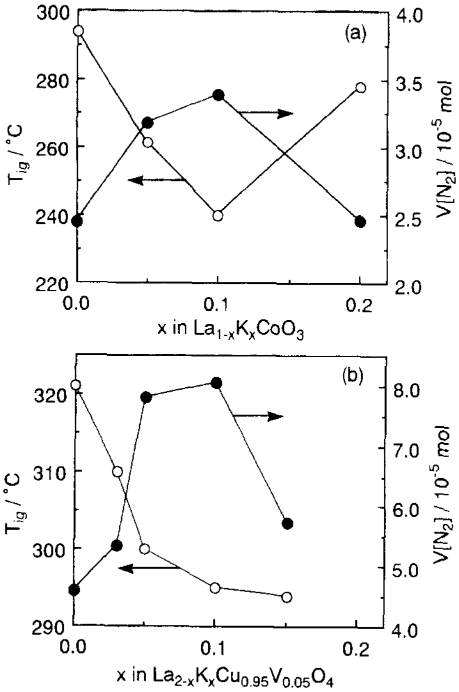

Fig. 4. Effect of the substitution of potassium for lanthanum on the ignition temperature of soot ($T_{ig}$) and the total amount of $N_2$ formed ($V[N_2]$). (a) $La_{1-x}K_xCoO_3$ and (b) $La_{2-x}K_xCu_{0.95}V_{0.05}O_4$.

als (lithium and cesium) but the effect of potassium was the most prominent. Depicted in Fig. 4 are the effect of the substitution level of potassium ($x$) for lanthanum on $T_{ig}$ and $V[N_2]$ in perovskite-type $La_{1-x}K_xCoO_3$ and K-type $La_{2-x}K_xCu_{0.95}V_{0.05}O_4$. In $La_{1-x}K_xCoO_3$ (a), the lowest $T_{ig}$ and the highest $V[N_2]$ are attained at $x=0.1$. In$La_{2-x}K_xCu_{0.95}V_{0.05}O_4$ (b), on the other hand, $T_{ig}$ tends to decrease monotonically with increasing $x$ and $V[N_2]$ becomes largest at $x=0.05$–$0.1$. These results show that the catalytic performance depends on the substitution level of potassium and the optimum substitution level is 0.1 in both oxide systems.

XRD investigation showed that $La_{1-x}K_xCoO_3$ and $La_{2-x}K_xCu_{0.95}V_{0.05}O_4$ crystallized in hexagonal and orthorhombic structures, respectively. Their unit cell volumes are plotted against the substitution level of potassium ($x$) in Fig. 5. Orthorhombic unit cell volume of K-type oxides, $V[K]_O$, decreased with an increase in $x$ and leveled off above $x=0.10$. The dependence of the hexagonal unit cell volume of perovskites, $V[P]_H$, was opposite to that of $V[K]_O$. From the simple geometric consideration, unit cells should expand by the substitution of larger potassium for smaller lanthanum. However, the substitution of monovalent $K^+$ for trivalent $La^{3+}$ also brings about the formation of oxide ion vacancies and/or the oxidation of $B$-site cations (Co or Cu) and they are expected to result in the shrinkage of the unit cell. Accordingly, the opposite dependence of unit cell volume on $x$ might be due to the predominance of the expanding or shrinking effect. The dependence of the unit cell volume on $x$ (Fig. 5) shows that the solubility limit of potassium is about 0.1 in both $La_{1-x}K_xCoO_3$ and $La_{2-x}K_xCu_{0.95}V_{0.05}O_4$. It can thus be concluded that the catalytic performance of these oxides increases as the amount of potassium in the crystal lattice increases. Beyond the solubility limit, on the other hand, excess potassium which is present on the surface of mixed metal oxides might deteriorate the catalytic performance.

### 3.3. Consideration to reaction mechanism

As discussed above for the effect of $B$-site cations, the decrease in $T_{ig}$ should correlate to the enhancement of the oxidation activity and actually $T_{ig}$ was found to decrease as the methane oxidation activity per surface area increased (Fig. 6). K-substituted oxides generally had smaller specific surface area than the corresponding Sr-substituted oxides (Table 1) but the specific oxidation activity per surface area of K-substituted oxides was

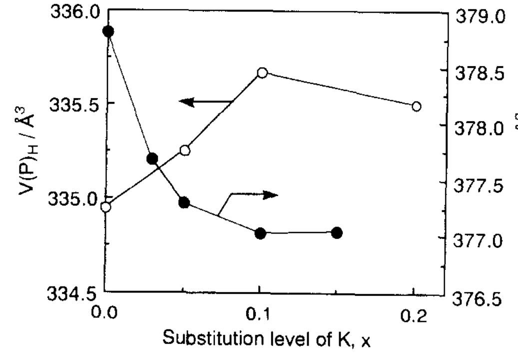

Fig. 5. Unit cell volume of hexagonal $La_{1-x}K_xCoO_3$, $V[P]_H$ and orthorhombic $La_{2-x}K_xCu_{0.95}V_{0.05}O_4$, $V[K]_O$, as a function of the substitution level of potassium ($x$).

higher than that of Sr-substituted oxides as demonstrated by a pair of oxides with Co (1–3) or $Mn_{0.8}Cu_{0.2}$ (13–14) at *B*-sites (Fig. 6). The simultaneous removal reaction of $NO_x$ and soot supposedly takes place at the so-called 'triple contact point' where the solid catalyst, the solid soot and the gaseous reactants ($NO_x$ and $O_2$) meet together. In such a case, the specific surface area may be of less importance than in the usual solid(catalyst)–gas(reactant) reaction. It has been reported that potassium enhances reactions in which carbon is concerned, such as gasification [6], combustion [7] and NO–C reaction [8–10]. Therefore it is speculated that the promotion effect of potassium in the present $NO_x$–$O_2$–soot reaction might be relevant to the nature of potassium to activate the surface of the soot. The origin of the effect of potassium in enhancing the selectivity should be made clear by future studies.

The parallelism between carbon dioxide and nitrogen formation rates in the Arrhenius-type plot (Fig. 2) indicates that the rate-determining step of carbon dioxide and nitrogen formation might be the same. It is also suggested that the selectivity to $NO_x$ reduction is independent of temperature; actually the selectivity calculated from the rates of carbon dioxide and nitrogen formation of $La_{1.9}K_{0.1}Cu_{0.95}V_{0.05}O_4$ (Fig. 2), 5.8%, is very close to that calculated from the total amounts of carbon dioxide and nitrogen formed, 5.9%.

Fig. 7 compares $T_{ig}$ of the selected oxides observed in reaction gases of NO (0.5%) + $O_2$ (5%), $O_2$ (5%) and NO (10%). $T_{ig}$ is dependent on the composition of reaction gases and decreases as NO > $O_2$ > NO + $O_2$. The lowest $T_{ig}$ in the NO + $O_2$ gas strongly suggests such a mechanism that the reaction is accelerated by the cooperation of nitric oxide and oxygen, e.g., the implication of nitrogen dioxide. It was reported that nitrogen dioxide oxidized diesel particulates more easily than oxygen [11].

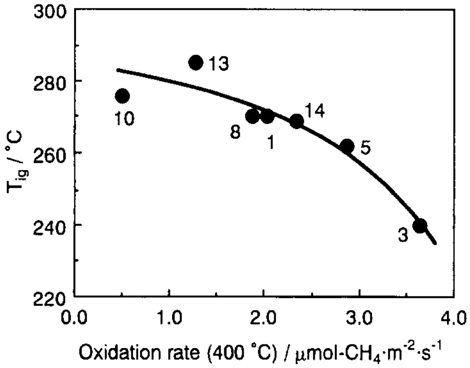

Fig. 6. Ignition temperature of soot ($T_{ig}$) as a function of methane oxidation activity per surface area at 400°C. See Table 1 for the listing of catalysts.

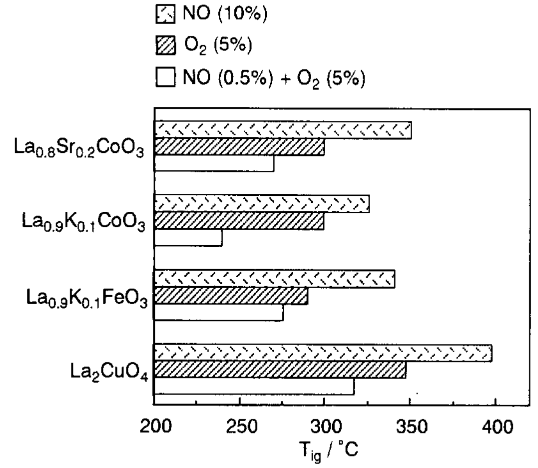

Fig. 7. Ignition temperature of soot ($T_{ig}$) observed in gaseous mixtures of NO + $O_2$, $O_2$ and NO.

## 4. Conclusions

The present investigation has revealed that perovskite-type and Cu-based $K_2NiF_4$-type oxides catalyze the simultaneous removal of $NO_x$ and diesel soot particulate and that these perovskite-related oxides are superior to transition metal simple oxides and $Pt/Al_2O_3$ with respect to the selectivity to $NO_x$ reduction. The catalytic activity evaluated from the ignition temperature of the soot and the selectivity to $NO_x$ reduction changed significantly by the sort and composition of *A*- and *B*-site cations. The most prominent promotion effect with the decreasing ignition temperature and the increasing selectivity was observed with the appropriate substitution of potassium for lanthanum at *A*-sites. The lowering of the ignition temperature correlated to the higher oxidation activity, while the origin of the effect of potassium in enhancing the selectivity may be relevant to the nature of potassium to activate the surface of soot. The dependence of the ignition temperature on the composition of reaction gases suggested the participation of nitrogen dioxide in the reaction. More detailed investigation on the reaction mechanism is now in progress in our laboratory.

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