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Preparation and characterization of $La_{1-x}K_xFeO_3$ ($x = 0–1$) by self-propagating high-temperature synthesis for use as soot combustion catalyst

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ABSTRACT

This paper proposes $La_{1-x}K_xFeO_3$ prepared by *self-propagating high-temperature synthesis* (SHS) as an alternative to platinum catalysts for promoting diesel soot combustion. The catalytic property of eleven products SHSed with different substitution ratios of potassium ($x = 0–1$) was experimentally evaluated using a thermobalance. In the mass loss curves of the product, T_{50} was defined as the temperature at which the weight of the reference soot decreases to half its initial weight. The BET specific surface area of SHSed $La_{1-x}K_xFeO_3$ depended on x strongly. All the products showed good oxidation catalytic activity. Despite having the smallest surface area ($0.11\ m^2/g$) among the obtained products, $La_{0.9}K_{0.1}FeO_3$ ($x = 0.1$) was found to be the best catalyst with the lowest T_{50} (442 °C). T_{50} of $La_{1-x}K_xFeO_3$ decreased with increasing x for $x > 0.2$. The products with $x = 0.6$ and 0.8 were the second-best catalysts in terms of their T_{50}. Moreover, average apparent activation energy of $La_{0.9}K_{0.1}FeO_3$ ($x = 0.1$) calculated by Friedman method using TG was as much as 61 kJ/mol lower than that of Pt/Al_2O_3 catalyst. In conclusion, potassium-substituted SHSed $La_{1-x}K_xFeO_3$ can be used as an alternative to Pt/Al_2O_3 for soot combustion.

1. Introduction

It is well known that *diesel engines* emit less carbon dioxide, a greenhouse gas, because of their high thermal efficiency and high durability. Further, they are more economical than gasoline engines. However, diesel exhaust gas contains two major pollutants: *particulate matter* (PM) and *nitrogen oxides* (NO_x). Diesel particulate filtering (DPF) and catalytic conversion, including soot combustion and selective catalytic reduction of NO_x, have been proposed to reduce the emission of these pollutants [1–4]. Noble-metal catalysts such as Pt, Rh, and Pd are mainly used for the combustion of PM accumulated in filters at low temperatures.

Perovskite-type oxides (ABO_3) are regarded to be one of the most promising alternatives to precious metal catalysts [5] such as Pt for the combustion of diesel PM. For example, the activity of $LaFeO_3$ is comparable to that of Pt/Al_2O_3 for methane, propane, and soot combustion. It is also known that the catalytic property of perovskite-type oxides drastically changes by the substitution of the elements in the A- or B-site of the ABO_3 structure with other elements [6]. $LaFeO_3$ is commonly obtained by the *Solid-State Reaction* (SSR) method along with a repeated heating procedure involving calcination and sintering. The SSR method is time and energy consuming because calcination and sintering require high-temperature heating for a long time [7,8]. *Self-propagating high-temperature synthesis* (SHS) has been reported to be highly effective for the mass production of $LaFeO_3$ [9–11]. Further, it can be used to obtain a homogeneous product with accurately controlled composition, which helps in minimizing the operating time and simplifying the procedure and equipment [10,11]. Because of the high reaction rate and high-temperature, this method can be used to synthesize materials that are difficult to synthesize by conventional methods.

Several previous studies have greatly contributed to the elucidation of the catalytic activity of potassium-substituted $LaFeO_3$ [12,13]. As mentioned before, conventional methods are not suitable for the mass production of perovskite-type oxides. The purpose of this study is to synthesize potassium-substituted $LaFeO_3$, a perovskite-type oxide ($La_{1-x}K_xFeO_3$; substitution ratio of potassium $x = 0–1$) by the SHS method. The obtained LKFx is expected to be as a catalyst for soot oxidation. The X-ray diffraction (XRD) analysis of the product phase, BET specific surface area, scanning electron microscope (SEM) observation, and soot combustion experiments for measuring the catalytic activity of the obtained products are mainly carried out by using a thermogravimetric analyzer (TGA). The findings of this study are expected to pave the way for designing new catalysts with applications in carbon combustion.

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Table 1
Properties of raw materials used for synthesizing LKFx (x = 0–1) by SHS.

Raw materials	Source	Particle diameter (μm)	Purity (mass%)
La_2O_3	Kojundo chemical	>10	99.9
K_2CO_3	Wako pure chemical industries	>10	99.9
Fe	Kojundo chemical	3–5	99.9
$NaClO_4$	Aldrich	>10	98

2. Experimental

2.1. Sample preparation

Properties and sources of the raw materials used for the synthesis of LKFx (x = 0–1) perovskite powders are listed in Table 1. Sodium perchlorate was selected as an oxidizing reagent for metallic iron and compensated for the oxygen deficiency [14,15].

The overall reaction involved in the SHS of LKFx (x = 0–1) is given as follows:

$$(0.5-0.5x)La_2O_3+0.5xK_2CO_3+Fe+(0.375+0.25x)NaClO_4 \rightarrow La_{1-x}K_xFeO_3+(0.375+0.25x)NaCl(g)+0.5xCO_2(g) \quad (1)$$

Fig. 1 shows the flow sheet for the synthesis of LKFx (x = 0–1) by the SHS method. First, La_2O_3, K_2CO_3, Fe, and $NaClO_4$ powders were roughly mixed in the desired ratio to obtain a total mass of 15 g. Then, the mixture was charged in an alumina pot with a diameter of 140 mm, containing 10 alumina balls of diameter 10 mm, for ball milling. The mill was operated at 60 rpm for 3 h under atmospheric conditions. Fig. 2 shows the schematic diagram of the experimental apparatus used for the SHS. The apparatus includes a reactor, a control unit, and a gas control system [16]. A heat-resistant glass window located at the top of the reactor enables the observation of real-time changes in the sample during the SHS. 10 g of the mixed raw materials was transferred to a graphite crucible ($30\,mm^W \times 30\,mm^H \times 75\,mm^L$), placed at the center of the SHS reactor. Prior to this, the reactor was evacuated by using a rotary pump and filled with argon gas (purity: 99.9%) at atmospheric pressure. The sample was ignited by using an electrically heated carbon foil ($5\,mm^W \times 200\,mm^L \times 0.1\,mm^T$) for 3 s. In SHS, the combustion wave, which moves out from the ignition point, rapidly propagates to the other end of the sample when one end is ignited, and the product with the desired composition is obtained in a short time. After the completion of ignition, the exhaust valve of the reactor was kept open for 20 min for the sample to cool down completely. The cooled sample was subjected to ultrasonic cleaning for the removal of NaCl. Then, the product was dried and ground in an agate mortar to obtain particles of sizes less than 25 μm.

The powders obtained by using the abovementioned method were characterized by X-ray diffraction (XRD) employing CuKα radiation (λ = 1.5418 Å). The specific surface area of the product was evaluated by using a BET analyzer (Autosorb 6AG, Yuasa Ionics) and the product surface was observed using an SEM.

2.2. Catalytic activity test

A TGA was used to examine the catalytic activity of the obtained catalyst for soot combustion. The test procedure was similar to that described in a previous report [16]; therefore, only the framework of test is described here. Samples were prepared by thoroughly mixing the catalyst and reference soot in the mass ratio of 9:1; carbon black powder (Printex® V, Degussa) was used as the reference soot. The properties of Printex® V are almost the same as those of Printex® U, except for the density, which is regarded to be chemically similar to that of actual diesel soot [17]. The product powders were mixed again in ethanol (under wet conditions) for 5 min using an ultrasonic homogenizer and then desiccated. Subsequently, 5 mg of the desiccated samples was analyzed in the TGA, in which they were heated to 700 °C at the rate of 3 °C/min at an air-flow rate of 50 ml/min. In the obtained mass loss curves, T_{50} was defined as the temperature at which the weight of soot decreased to half its initial weight. Pt/Al_2O_3 (JRC-PTAL-1; Pt: 1 mass%; Nikki-Universal Co., Ltd.) was also used as a reference for evaluating the catalytic activity of the obtained catalyst for soot combustion.

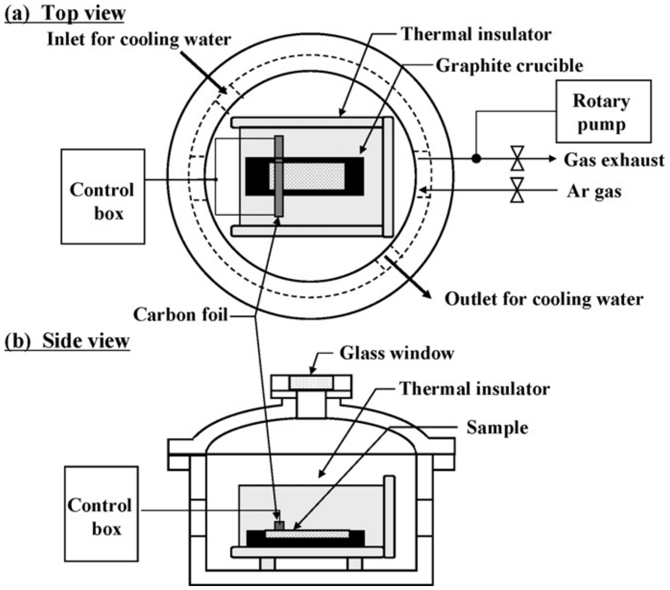

Fig. 2. Schematic diagram of SHS experimental apparatus used for synthesizing perovskite catalysts [16]. The ignition, propagation of the reaction wave, and completion of reaction can be observed through the glass window.

3. Results and discussion

3.1. Characteristics of SHSed $La_{1-x}K_xFeO_3$

Fig. 3 shows XRD patterns of LKFx (x = 0–1) samples synthesized by the SHS method. LKF00 (x = 0) corresponded to the $LaFeO_3$ phase [18(a)]. As expected, the products exhibited the perovskite phase, except the product with x = 1. No peaks of the unreacted raw materials were detected in the products. The peaks of perovskite became smaller with increasing potassium substitution ratio, x, whereas those of the byproducts became larger with increasing x. The byproducts were formed above x = 0.3, however, it was not clear less than x = 0.6. According to the JCPDS database, the peaks of

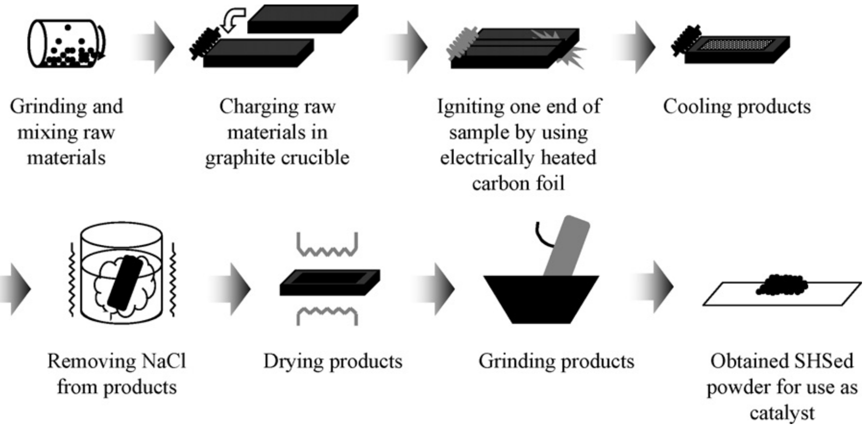

Fig. 1. Schematic illustration of *self-propagating high-temperature synthesis* (SHS) method for preparing perovskite catalysts. In this method, oxides, carbonates, and $NaClO_4$ are mixed thoroughly and then ignited.

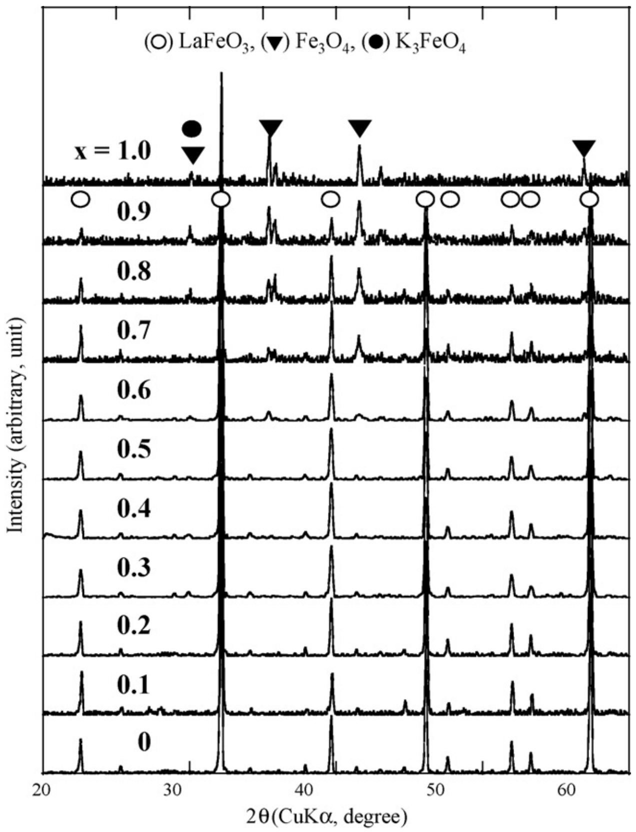

Fig. 3. X-ray diffraction (XRD) patterns of $La_{1-x}K_xFeO_3$ ($x = 0.1–1.0$) synthesized by SHS method. This figure shows major peaks of $LaFeO_3$.

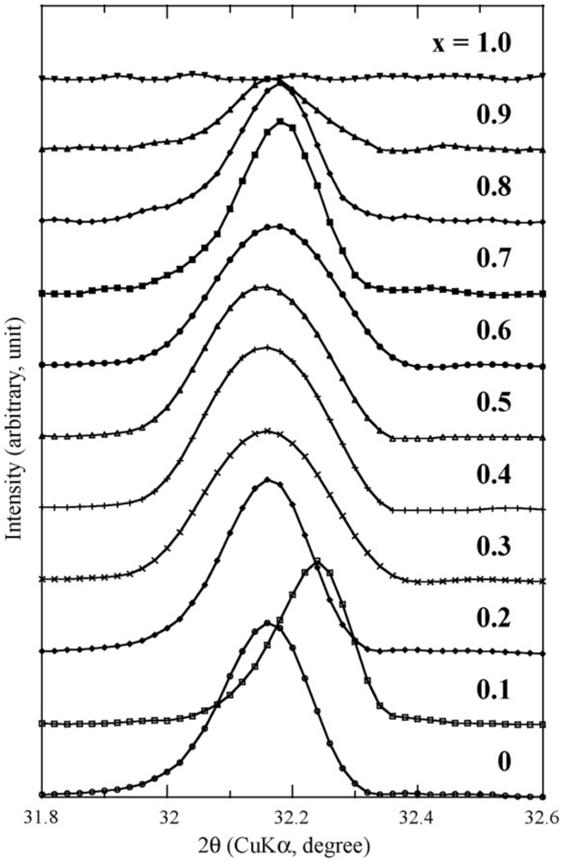

Fig. 4. Enlarged XRD patterns of SHSed $La_{1-x}K_xFeO_3$ ($x = 0.1–1.0$) from 31.8° to 32.6°.

byproducts were assigned to the Fe_3O_4 phase [18(b)] and K_3FeO_4 phase [18(c)]. The byproducts were formed due to the decrease in the adiabatic flame temperature, caused by the increase in the amount of K_2CO_3 in the raw material. This is probably because the decomposition energy of K_2CO_3 is larger than that of La_2O_3. Therefore, the product with a large x tended to contain more byproducts.

Fig. 4 shows enlarged XRD patterns ($31.8° < 2\theta < 32.6°$) of LKFx ($x = 0–1.0$) samples synthesized by the SHS method. In the case of LKF01, the peak of the perovskite phase was observed at 32.22°, whereas in the case of other products, the peaks were observed in the range of 32.14–32.16°. These results indicate that the unit cells of LKF01 shrank because of the substitution of lanthanum with potassium. Generally, such a substitution causes the expansion of unit cells since the ion radius of potassium is larger than that of lanthanum. However, as reported in a previous paper, the substitution of trivalent La^{3+} with monovalent K^+ leads to the formation of oxide ion vacancies and/or the oxidation of B-site cations. As a result, the unit cells of LKF01 shrank. Accordingly, the opposite dependence of the unit cell volume on x might be due to the predominance of the expansion or shrinkage effect [12]. Thus, it appears that lanthanum was substituted with potassium only in LKF01.

Fig. 5 shows the specific surface area (m^2/g) of SHSed LKFx ($x = 0–1$) catalysts measured by the BET method. The x axis represents the substitution ratio of K in SHSed LKFx ($x = 0–1$). Data for non-catalyzed soot combustion and Pt/Al_2O_3 (1 mass% Pt) are also shown for reference. LKF00 had a particularly small specific surface area ($0.89\,m^2/g$). This could be explained by the fact that the BET surface area of perovskite obtained by conventional methods is generally in the range of $1–10\,m^2/g$ [19]. However, the specific surface areas of the SHSed $La_{1-x}K_xFeO_3$ perovskite obtained in this study, $0.110–10.3\,m^2/g$, were considerably smaller than the conventional values. For example, LKF01 had the smallest specific surface area, $0.110\,m^2/g$, and LKF03, the largest specific area, $10.3\,m^2/g$. The specific surface area of the reference catalyst, Pt/Al_2O_3, $176\,m^2/g$, was significantly larger than that of SHSed LKFx.

Fig. 6(a) shows SEM images of the SHSed $La_{0.9}K_{0.1}FeO_3$ crystals. Fig. 6(b) shows that the major product of SHSed LKF01 was orthorhombic in shape. LKF01 exhibited high crystallinity because $LaFeO_3$ has an orthorhombic perovskite structure [18(a)]. LKF01

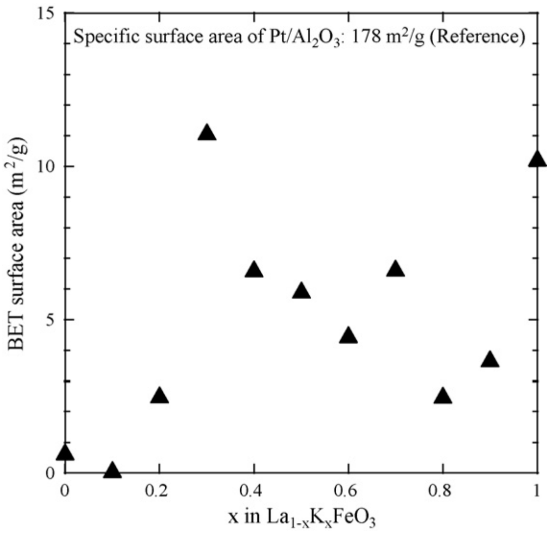

Fig. 5. Specific surface area of SHSed $La_{1-x}K_xFeO_3$ ($x = 0–1$) catalysts, measured by BET method. The x axis shows the substitution ratio of potassium in SHSed $La_{1-x}K_xFeO_3$ ($x = 0–1$). The commercially available Pt/Al_2O_3 (1 mass% Pt) catalyst has a large specific surface area of $178\,m^2/g$.

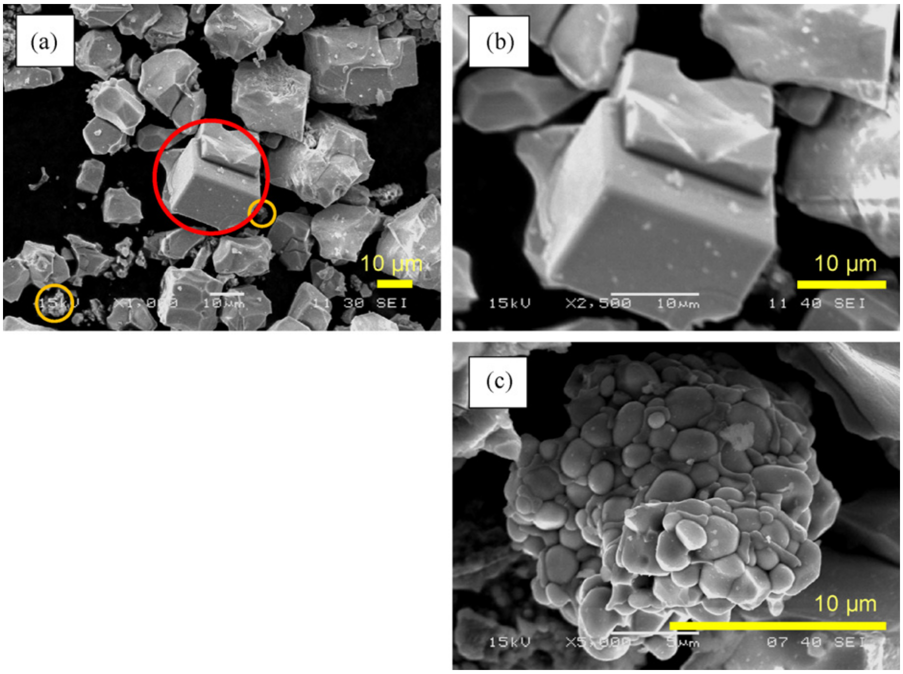

Fig. 6. SEM images of (a) SHSed $La_{0.9}K_{0.1}FeO_3$ crystals and $La_{0.9}K_{0.1}FeO_3$ with (b) orthorhombic shape and (c) irregular shape. The scale bar is 10 μm.

required high-temperature for the formation the orthorhombic structure. Fig. 6(c) shows that the minor products of LKF01 were irregular in shape. This result suggests that the temperature was not sufficiently high for the minor products to form an orthorhombic structure. This is probably because the decomposition energy of K_2CO_3 is larger than that of La_2O_3, resulting in the decrease in the adiabatic flame temperature. Therefore, a minor amount of irregularly shaped products are obtained.

3.2. *Catalytic activity of LKFx*

Fig. 7 shows results of the soot combustion experiments carried out using the TGA. The *x* axis represents the substitution ratio of K in SHSed LKF*x* ($x = 0–1$), non-catalyzed soot combustion, and Pt/Al_2O_3 (1 mass% Pt), and the *y* axis represents T_{50}. The smaller the value of T_{50}, the higher is the catalytic activity because a low T_{50} implies that the catalyst burns soot at a low temperature and it has high catalytic activity for soot combustion. Accordingly, LKF00 exhibited a low catalytic activity, while LKF01 exhibited a high catalytic activity. All the LKF*x* ($x = 0–1$) samples exhibited high catalytic activity for soot combustion. Further, comparison with the data of non-catalytic soot combustion shows that the combustion efficiency increased with the use of these catalysts. The soot combustion activity is generally affected by physical and chemical factors such as the specific surface area and the amount of oxygen desorbed from the surface of the catalyst [20,21].

LKF01 with $T_{50} = 441$ °C exhibited the highest activity for soot combustion. This value of T_{50} was 125 °C less than that in non-catalytic combustion (566 °C). Despite having the smallest specific surface area among the obtained products, LKF01 exhibited the highest catalytic activity. This was probably because potassium-substituted perovskite-type oxides generally have a small specific surface area but a high specific oxidation activity per surface area [22].

On the other hand, LKF02 showed low catalytic activity for soot combustion. It has been reported that potassium present in the lattice of catalysts promotes the catalytic activity [22], but excess potassium present on the surface of mixed metal oxides might decrease the activity [12]. Therefore, we speculated that in the case of LKF01, potassium was present in the lattice, and in case of LKF02, potassium was present on surface, and not in the lattice.

Moreover, above $x = 0.2$, the catalytic activity for soot combustion increased with *x*. In particular, LKF06 and LKF08, with T_{50} of 446 °C and 447 °C, respectively, exhibited high activity for soot combustion. The La–K–Fe–O system is the dominant phase with small amounts of potassium iron oxide (K–Fe–O) and iron oxide (Fe–O) [13]. These byproducts also contributed to the increase in the catalytic activity for soot combustion [22].

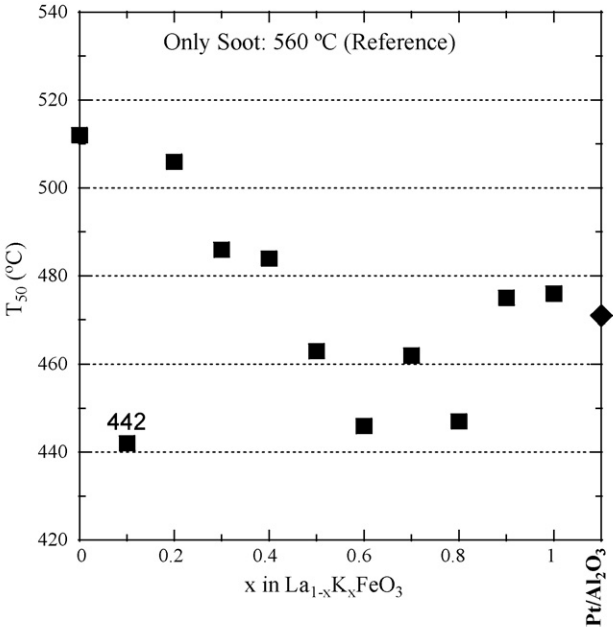

Fig. 7. Soot combustion temperature T_{50} against substitution ratio of potassium, *x*, in SHSed $La_{1-x}K_xFeO_3$ ($x = 0–1$). Data of soot combustion without any catalysts and data of the commercially available Pt/Al_2O_3 catalyst (1 mass% Pt) are shown for reference. T_{50}: the temperature at which the soot weight becomes 50% of the initial value.

Table 2
Summary of the averaged apparent activation energy for soot combustion with/without catalyst.

Catalyst	$f = 0.75$		$f = 0.50$		$f = 0.25$		E_{AV} (kJ/mol)
	$E_{0.75}$ (kJ/mol)	R^2	$E_{0.50}$ (kJ/mol)	R^2	$E_{0.25}$ (kJ/mol)	R^2	
Non-catalyzed soot	166	0.999	177	0.999	185	1.00	176
Pt/Al_2O_3	138	0.999	167	0.999	172	0.999	159
$LaFeO_3$	140	0.999	159	0.999	145	0.999	148
SHSed $La(K)FeO_3$							
$La_{0.9}K_{0.1}FeO_3$	118	0.993	109	1.00	127	0.988	118
$La_{0.8}K_{0.2}FeO_3$	167	0.978	176	0.954	172	0.994	172
$La_{0.7}K_{0.3}FeO_3$	113	0.999	133	0.997	146	0.993	131
$La_{0.6}K_{0.4}FeO_3$	120	0.994	133	1.00	135	1.00	129
$La_{0.5}K_{0.5}FeO_3$	126	0.999	140	1.00	136	0.991	134
$La_{0.4}K_{0.6}FeO_3$	122	1.00	129	1.00	130	1.00	127
$La_{0.3}K_{0.7}FeO_3$	137	0.995	134	1.00	146	0.999	139
$La_{0.2}K_{0.8}FeO_3$	131	0.996	126	0.995	136	0.991	131
$La_{0.1}K_{0.9}FeO_3$	149	0.983	143	0.991	138	0.995	143
$La_{0.0}K_{1.0}FeO_3$	132	0.986	133	0.972	144	0.954	137

In order to understand the combustion of soot from reaction kinetics, the activation energy of soot combustion on the sample with/without catalysts was evaluated according to well known *the Friedman method* by using TG equipment [23,24]. This method is that apparent kinetic parameters are derived from weight loss curve.

Based on this methodology, the value of E for soot combustion with catalysts in all experiments was calculated. Table 2 gives summary of the averaged apparent activation energies for soot combustion with/without catalyst; that is, only soot without catalyst, Pt/Al_2O_3, SHSed $LaFeO_3$, SHSed $La(K)FeO_3$ were evaluated, where a value of R^2 is a determination coefficient.

Table 2 indicates that the averaged apparent activation energy for SHSed $La(K)FeO_3$ were 118–172 kJ/mol, which are lower than that of non-catalytic soot combustion, 176 kJ/mol. It is well known that the soot combustion activity, expressed by small activation energy, is generally caused by physical and chemical factors such as the specific surface area and desorbed oxygen from the surface of the catalyst [20,21]. Furthermore, it is reported that the amount of desorbed oxygen increases with increasing the K substitution ratio, x, in $La_{1-x}K_xFeO_3$ [13]. The results indicate that the soot combustion activity of SHSed catalyst was enhanced by K substitution. The averaged activation energy for the commercially-produced Pt/Al_2O_3 catalyst was 159 kJ/mol; in contrast, the activation energies for SHSed $La_{1-x}K_xFeO_3$ except for $x = 0.2$ became lower than that of Pt/Al_2O_3 catalyst, as expected. The results revealed that SHSed catalysts of $La_{1-x}K_xFeO_3$ except for $x = 0.2$ had the superior activity to Pt/Al_2O_3 catalyst on the soot combustion from the viewpoint of smaller activation energy. These results show that although LKF01 has a small specific surface area and is not as good as the platinum catalyst, it has relatively high catalytic activity for soot combustion.

4. Conclusion

In this study, potassium-substituted $LaFeO_3$ perovskite samples ($La_{1-x}K_xFeO_3$) were prepared by the SHS method, and their catalytic activity for soot combustion was evaluated using a TGA, in comparison to the commercially available catalyst, Pt/Al_2O_3 (1 mass% Pt).

The results obtained are as follows:

(1) Interestingly, the specific surface area of the products, LKFx, strongly depended on the x value; the area ranged from 0.11 m^2/g for $x = 0.1$ to 10 m^2/g for $x = 0.3$.
(2) The catalytic activity of the obtained products was quantitatively evaluated from their T_{50}; the smaller the value of T_{50}, the higher is the activity of a catalyst for soot combustion. Although LKF01 had the smallest specific surface area of 0.11 m^2/g among the obtained products, it was the best catalyst for soot combustion having the lowest T_{50}, 442 °C.
(3) For $x > 0.2$, T_{50} of the products decreased. T_{50} of LKF06 and LKF08 were 446 °C and 447 °C, respectively.
(4) Potassium substitution of La in $LaFeO_3$ was quite effective for improving the oxidative activity for soot combustion. The SHSed $La_{1-x}K_xFeO_3$ showed increased activity of soot combustion with the increasing K substitution ratio, x, except for $x = 0.2$. The value of 0.1 as x gave the most active among the series of $La_{1-x}K_xFeO_3$. The value of the average activation energy of soot combustion was only 118 kJ/mol for $La_{0.9}K_{0.1}FeO_3$.

The results also suggest that the catalytic activity of LKF01 would be much improved by increasing its surface area.

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