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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 LKF*x* ($x = 0$–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 LKF*x* ($x = 0$–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 LKF*x* ($x = 0$–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 LKF*x* ($x = 0$–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 × 30 mm^H × 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 × 200 mm^L × 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.

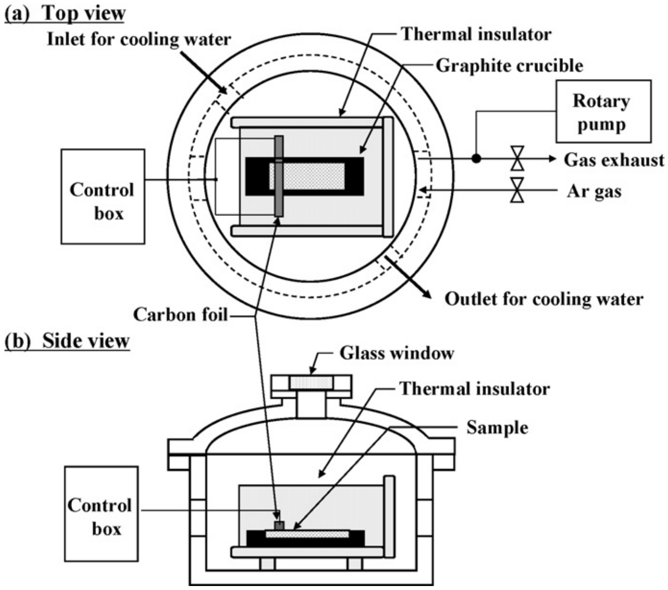

Fig. 2. Schematic diagram of SHS experimental apparatus used for synthesizing perovskite catalysts [16]. The ignition, propagation of the reaction wave, and completion of reaction can be observed through the glass window.

3. Results and discussion

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

Fig. 3 shows XRD patterns of LKF*x* ($x = 0$–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

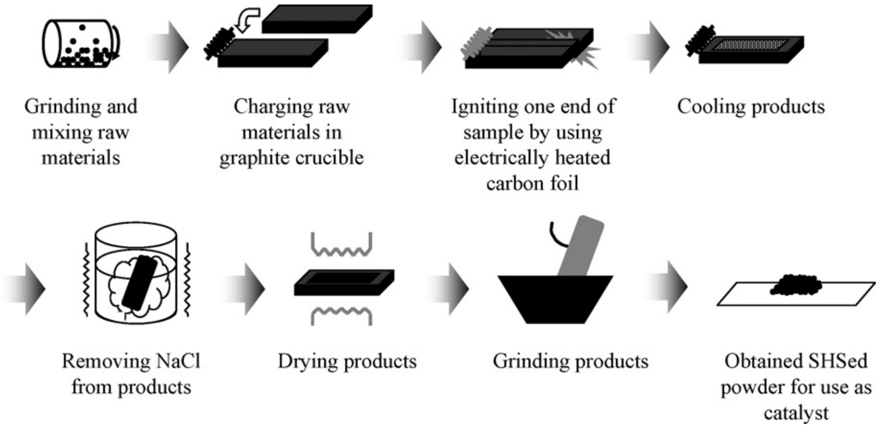

Fig. 1. Schematic illustration of *self-propagating high-temperature synthesis* (SHS) method for preparing perovskite catalysts. In this method, oxides, carbonates, and $NaClO_4$ are mixed thoroughly and then ignited.