O U R N A L O F

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Solution combustion synthesis and surface properties of LaFeO₃ powders

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LaFeO₃ powders were prepared by solution combustion synthesis (SCS) using citric acid as a fuel and metal nitrate as an oxidizer. By a simple procedure the mixed solution was held at 400 °C for 10 minutes, and single-phase perovskite-type LaFeO₃ oxide powders with good crystallinity were obtained for lean fuel compositions where the fuel–oxidizer ratio (ϕ) was less than 1.0. Two species of oxygen, namely lattice oxygen and adsorbed oxygen, appeared in the deconvolution of O 1s photoelectrons measured by X-ray photoelectron spectroscopy (XPS). It was found that the activation energy for the soot combustion of the synthesized LaFeO₃ powders was closely related to the ratio of the two oxygen states. The best catalytic activity for soot combustion was obtained for LaFeO₃ powders synthesized from the $\phi = 0.6-0.7$ compositions where the ratio of adsorbed oxygen-to-lattice oxygen was a maximum.

Key words: Solution combustion synthesis, soot combustion, X-ray photoelectron spectroscopy, thermal properties.

Introduction

Perovskite-type mixed metal oxides exhibit a wide range of defect-related phenomena especially when first transition series elements like iron are incorporated. Electrons can be easily added to or removed from iron, and several valence states can appear according to the synthetic conditions [1]. Perovskite-type mixed metal oxides are potential candidates as catalysts for the combustion of particulate matters emitted from diesel engines because they show good thermochemical stability and catalytic activity [2-4].

Perovskite-type oxides are prepared by numerous wet chemical procedures such as sol-gel synthesis, the polymerizable complex method, co-precipitation, the citrate method and freeze-drying [5-7]. We prepared LaFeO₃ powders by solution combustion synthesis (SCS). This is a novel one-step procedure in which well-ordered crystalline monophase oxide powders are obtained by choosing optimum synthesis parameters such as ambient atmosphere and fuel-oxidizer ratio [8, 9]. SCS has many advantages such as low-cost starting materials (metal nitrates), a simple procedure and a very low synthesis temperature owing to the self-sustaining exothermic reaction. In a SCS reaction, organic fuel plays multiple roles: it reacts with metal precursors and offers good solution homogeneity without precipitation by forming complexes with metal cations.

In this paper, the solution combustion behavior of the starting materials, phases, microstructures, catalytic activity for the soot combustion reaction and surface properties of the synthesized powders were investigated. The soot combustion reaction is closely related to the surface properties of the powders. Two oxygen 1s states which depend on the ratio of fuel-to-metal nitrate during synthesis appeared and they were responsible for the carbon combustion catalytic activity.

Experimental

LaFeO₃ powders were synthesized by SCS using citric acid as an organic fuel and metal nitrate as a metal precursor (oxidizer). Equation (1) shows the overall solution combustion reaction. Here ϕ denotes the citric acid-to-metal nitrate ratio, and it varied from 0.5 to 1.2:

$$Fe(NO_{3})_{3} \cdot 9H_{2}O + La(NO_{3})_{3} \cdot 6H_{2}O + 2\left(\phi - \frac{1}{6}\right)C_{6}H_{8}O_{7}$$
$$+9(\phi - 1)O_{2} \rightarrow LaFeO_{3} + 12\left(\phi - \frac{1}{6}\right)CO_{2}$$
$$+\left(8\phi + \frac{41}{3}\right)H_{2}O + 3N_{2}.$$
(1)

The desired amounts of iron nitrate nonahydrate, $Fe(NO_3)_3 \cdot 9H_2O$ (Riedel-deHaen, 97%), lanthanum nitrate hexahydrate, La(NO₃)₃·6H₂O (Fluka, 99%), and citric acid, $C_6H_8O_7$ (Fluka, 99%), were completely dissolved in 5 ml of distilled water in a ceramic dish. The prepared aqueous solution was dried on a hot plate. The dried sample was put into an electric furnace preheated at 400 °C and held for 10 minutes in an ambient atmosphere to ignite the solution combustion reaction.

The SCS reaction temperature of the dried sample was analyzed by differential thermal analysis (DTA) and thermo-

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gravimetry (TG) using a Shimadzu TA-50 thermal analysis instrument. The phases of the synthesized powders were characterized by an X-ray diffractometer (XRD) using a Rigaku diffractometer (D/max-IIIC) equipped with Cu Ka radiation at an acceleration voltage of 30 kV and at a sample current of 30 mA. The microstructure of powders was observed by a scanning electron microscope (SEM) using a Jeol JSM-6700F model. The surface composition and oxygen states were measured by XPS using a VG Escalab 250 spectrometer with an Al K α source. The spectra were obtained at a pass energy of 20.0 eV, resolution of 0.7 eV and step of 0.1 eV. The activation energy of LaFeO₃ powders during soot combustion was obtained by DTA using the Ozawa method [10]. The reaction mixture was prepared by grinding the as-synthesized LaFeO₃ powders in an alumina agate until the average particle size reached ca. 1.5 µm and by mixing them with 10 wt% of artificial soot (Printex-U, Degusa). The activation energies were calculated from DTA exothermic peak temperatures at various heating rates (5, 10, 20, 30 and 50 K \cdot minute⁻¹) with an air flow of 50 ml minute⁻¹.

Results and Discussion

In an SCS reaction a stoichiometric fuel-oxidizer ratio is defined as $\phi = 1$. This is the situation where LaFeO₃ can be formed without additional oxygen, while $\phi > 1$ ($\phi < 1$) implies a fuel-rich (lean) condition. Fig. 1 shows the DTA results of the dried starting material. The exothermic reactions by solution combustion appear as very sharp peaks at the temperature range of 164-173 °C. These temperatures correspond to the initiation of the fuel combustion. As the amount of fuel decreases (as ϕ decreases) the exothermic peak shifts to a higher temperature. Abrupt weight decreases are also found in the TG analysis at approximately the same temperature range. It is notable that the initiating temperature of SCS is low compared with other preparation methods. This enables us to synthesize LaFeO₃ powders at a relatively low temperature.



Fig. 1. DTA analysis curves of the solution mixture during the combustion reaction.



Fig. 2. XRD patterns of the LaFeO₃ powders synthesized by solution combustion with various values of ϕ .

In the XRD patterns of the synthesized LaFeO₃ powders (Fig. 2), well-defined diffraction peaks are found for the lean fuel compositions. When excess fuel was added the diffraction peaks became small. The TG analysis for the synthesized powders showed that 18 wt% loss occurred up to 700 °C for the $\phi = 1.2$ composition because of the remaining carbon residues. No weight loss was found for ϕ under 0.8.

Fig. 3 shows the microstructure of the as-synthesized LaFeO₃ powders. Small crystallites are found being agglomerated to form powders for the $\phi = 0.6 - 0.8$ compositions. For the $\phi = 0.8$ composition it is seen that the size of the primary particle is smaller than that of the $\phi = 0.6$ and $\phi = 0.7$ compositions, and the primary particles are intensively sintered. In contrast, the powders obtained from the $\phi = 0.5$ composition show no sign of primary particles. From XRD patterns and SEM images, powders obtained from the $\phi = 0.6$ and $\phi = 0.7$ compositions show good crystallinity and clear primary particle shapes. Organic fuel was insufficient to complete the LaFeO₃ phase formation by combustion for the $\phi = 0.5$ composition. For the compositions above $\phi = 0.8$ organic fuel may exist excessively, which influences the shape and crystalline nature of the powders.

The activation energies for the soot combustion are shown in Table 1. The activation energies of powders Solution combustion synthesis and surface properties of LaFeO₃ powders

Fig. 3. SEM images of the LaFeO₃ powders synthesized by solution combustion. The scale bar is 1 μ m.

Table 1. Activation energies for soot combustion, and atomic percentage concentrations derived from XPS deconvolution analysis of the LaFeO₃ powders

	Activation energy, E _a (kJ/mol)	Atomic concentration (%)		
		O _{lattice}	Oadsorbed	O _{adsorbed} /O _{lattice} ratio
φ = 0.5	136.5 ± 0.4	66.76	12.18	0.18
$\phi = 0.6$	99.7 ± 0.2	50.06	25.35	0.51
$\phi = 0.7$	102.6 ± 0.2	45.52	25.04	0.55
$\phi = 0.8$	$111.1 \pm ZZ1.1$	56.63	18.55	0.33

from all ϕ values were lower than those of non-catalytic oxides [2, 11]. It is known that the solid-solid wetting is a possible mechanism for soot combustion [12]. The tightness of contact between oxides and soot is important for the reaction. Because the particle size of the LaFeO₃ was controlled to be nearly uniform by grinding, the variation in activation energy for different ϕ derives from the surface properties of the LaFeO₃ powders. The influence of the specific area of the powders is not significant as soot combustion results from solid-solid contact, not from gas-solid contact.

Fig. 4 shows the XPS spectra in the O 1s region of LaFeO₃ powders. In the deconvolution of O 1s spectra, four types of emitted electrons appear. The peaks at around 528.4-528.8 eV and 530.4-530.8 eV originate from the

oxygen of LaFeO₃. The peak at a higher binding energy than the oxygen species comes from the hydroxide due to adsorbed water molecules, and that at a lower energy comes from a charging effect. It is known that two types of oxygen species can be distinguished at the perovskitetype metal oxide surfaces [1, 2, 13]. One is lattice oxygen $(O_{lattice})$ that usually exists as an O^{2-} ion. The other is adsorbed oxygen (Oadsorbed) that easily changes into various states having different negative charges. The O 1s binding energy of adsorbed oxygen appears at a higher energy than that of the lattice oxygen because adsorbed oxygen is loosely bound to the solid surface. The adsorbed oxygen desorbs in the temperature range of 300-600 °C, and the lattice oxygen desorbs at a higher temperature [14]. It is possible for adsorbed oxygen to spill over the soot surfaces in contact with oxides [15]. This increases the number of reaction sites and enhances the reaction kinetics. Therefore the soot combustion activity of LaFeO₃ powders depends on the surface concentration of active oxygen species. Atomic concentrations of the two oxygen species and their ratios are shown in Table 1. From the table the minimum activation energy is obtained at $\phi = 0.6$, and the maximum $O_{adsorbed}/O_{lattice}$ ratio is obtained at $\phi = 0.7$. It is clear that precise control of the fuel-oxidizer ratio is necessary to achieve good catalytic activity even though LaFeO₃ powders may have been characterized as single phase from XRD patterns. In the SCS of LaFeO₃ powders,



Fig. 4. X-ray photoelectron spectra in the O Is region of the LaFeO₃ powders synthesized by solution combustion and their deconvolution.

it is found that a fuel-metal nitrate ratio of 0.6-0.7 is optimum for the preparation of a soot catalyst.

Conclusions

Perovskite-type single-phase LaFeO₃ powders were synthesized by a solution combustion method using a metal nitrate and citric acid. Under a lean fuel condition where the ratio of fuel-to-metal nitrate is less than 1.0, a well-ordered crystalline structure and small primary particles were obtained. From the activation energy measurements for soot combustion and the deconvolution of oxygen 1s photoelectrons, it was found that a fuel-metal nitrate ratio of 0.6-0.7 was best for the soot combustion reactivity of LaFeO₃ powders.

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References

- 1. Ü. Kersen, Analyst 126 (2001) 1377-1381.
- 2. N. Russo, D. Fino, G. Saracco and V. Specchia, J. Catal. 229 (2005) 459-469.
- S. Ponce, M.A. Pe and J.L.G. Fierro. Appl. Catal. B: Environ. 24 (2000) 193-205.
- M. Sadakane, T. Asanuma, J. Kubo and W. Ueda. Chem. Mater. 17 (2005) 3546-3551.
- 5. S. Bilger, G. Blass and R. Förthmann, J. Eur. Ceram. Soc. 17 (1997) 1027-1031.
- M. Popa, J. Frantti and M. Kakihana. Solid State Ion. 154-155 (2002) 437-445.
- J. Kirchnerova and D. Klvana, Solid State Ion. 123 (1999) 307-317.
- K. Deshpande, A. Mukasyan and A. Varma, Chem. Mater. 16 (2004) 4896-4904.
- S. Specchia, A. Civera and G. Saracco, Chem. Eng. Sci. 59 (2004) 5091-5098.
- 10. T. Ozawa, J. Therm. Anal. 2 (1970) 301-24.
- 11. M.A. Hasan, M.I. Zaki, K. Kumari and L. Pasupulety, Thermochim. Acta 320 (1998) 23-32.
- J. Harber, T. Machej and T. Czeppe, Surf. Sci. 151 (1985) 301-310.
- T. Seiyama, in J. Nowotny, L-C. Dufour (Ed.), "Surface and Near-surface Chemistry of Oxide Materials" (Amsterdam, Elsevier, 1988) pp. 189-217.
- 14. N. Yamazoe, Y. Teraoke, Catal. Today 8 (1990) 175-199.
- B.A.A.L. van Setten, M. Makkee and J.A. Moulijin, Catal. Rev. Sci. Eng. 43 (2001) 489-564.