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Mechanical Activation of Self-Propagating High-Temperature-Synthesized LaFeO₃ to Be Used as Catalyst for Diesel Soot Oxidation

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Abstract(50)

We proposed active catalyst of SHSed LaFeO_3 (LFO) as alternatives to precious metals such as platinum for promoting the oxidation of diesel particulate matter (PM). Significantly, the LFO samples exhibited good catalytic activity for the oxidation of carbon black, though their surface area was smaller than that of $\text{Pt/Al}_2\text{O}_3$.

Keywords: Self-propagating high-temperature synthesis; Lanthanum iron oxide; Mechanical activation; Catalyst; Soot oxidation

1. Introduction

Diesel engines emit less quantities of carbon dioxide (a well-known greenhouse gas), have high thermal efficiency, and high durability; as a result, they are more economical than gasoline engines. However, diesel exhaust gas contains two major pollutants: (i) particulate matter (PM), which largely consists of soot, soluble organic fractions (SOF), and sulfur, and (ii) nitrogen oxides (NO_x). To curb the emission of these pollutants several methods such as exhaust-gas recirculation (EGR), high-pressure fuel injection (employed in common-rail systems), diesel particulate filter (DPF) and catalytic conversion (including soot oxidation and selective catalytic reduction of NO_x) have been proposed [1, 2]. Noble-metal catalysts such as platinum-supported alumina ($\text{Pt}/\text{Al}_2\text{O}_3$) are mainly used for smooth oxidation of particulate matter accumulated in filters.

Perovskite-type oxides are regarded to be one of the alternatives to precious metal catalysts such as Pt for the oxidation of diesel particulate matter. In particular, LaFeO_3 (LFO) is known to be a good catalyst for soot oxidation. However, LFO is commonly obtained by using the solid-state reaction method, which consumes a large amount of time and energy because the starting mixture has to be heated at high temperatures during calcination and sintering [3, 4]. To avoid sintering at high temperatures, conventional wet chemical syntheses such as the amorphous citrate process (Pechini method) and sol-gel method have been adopted to synthesize LFO. However, these methods involve the use of expensive starting materials and complex procedures [5, 6]. For these reasons, the abovementioned conventional methods are not suitable for the mass production of LFO.

Self-propagating high-temperature synthesis (SHS) has been reported to be highly effective for the mass production of LFO. This method has several advantages such as a low operating time and requirement of simple equipment [7–9]. However, because of its small specific surface area (only $0.89 \text{ m}^2/\text{g}$), LFO obtained by SHS exhibits lower activity for oxidation than does the conventional $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst. Therefore, the purpose of this study is to subject LFO obtained from SHS to mechanical activation (MA) in order to improve the catalytic activity for soot oxidation. In particular, the effect of milling time on the diameter of the LFO particles, the BET surface area, and catalytic activity of the LFO obtained from SHS were mainly studied. The findings of this study can be used to develop industrial catalysts for the oxidation of soot emitted from diesel engines.

2. Experimental

2.1. Preparation and characterization of the catalyst

The characteristics and sources of raw materials used for the synthesis of perovskite oxide powders are listed in Table 1. NaClO₄ powder was chosen to oxidize metallic Fe [10]. The reaction involved in the SHS of LFO is as follows:



Table 1 Properties of the raw materials from which LFO is synthesized.

Raw materials	Source	Particle diameter (μm)	Purity (mass%)
La ₂ O ₃	Kojundo Chemical	>10	99.9
Fe	Kojundo Chemical	3–5	99.9
NaClO ₄	Aldrich	>10	98

La₂O₃, Fe, and NaClO₄ powders in the desired mixing ratio were thoroughly mixed, and then, 50 g of the mixed powder was placed in an alumina ball mill of diameter 140 mm containing 10 alumina balls, each of diameter 10 mm. The ball mill was operated at 60 rpm for 3 h under atmospheric conditions.

Fig. 1 shows the schematic diagram of the experimental apparatus used for SHS. The apparatus includes a reactor, a control unit, and a gas control system [11]. A heat-resistant glass window located at the top of the reactor allows the observation of real-time changes in the sample during SHS. Firstly, 10 g of the sample powder was poured into a graphite crucible (30 mm^W × 30 mm^H × 75 mm^L), which was 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 an electrically heated carbon foil (5 mm^W × 200 mm^L × 0.1 mm^T) for 3 s. After the ignition was completed, the exhaust valve of the reactor was kept open for 20 min to allow the sample to cool down completely. The cooled sample was subjected to ultrasonic cleaning for the removal of NaCl. Then, the product was ground in an agate mortar to obtain particles of sizes less than 0.1 mm.

The obtained LFO powders were milled at the speed of 500 rotation per minute (RPM) in the inclined planetary ball mill (GOKIN Ltd., PLANET) for different milling periods from 0.5 to 6 h. Samples in which the mass ration between LFO (in terms of mass ratio), zirconium oxide balls (diameter: 0.5 mm), and water (dispersion media) was 1: 9: 1 were placed in a zirconium oxide pot. Using the inclined planetary ball mill, samples could be milled to obtain powders of any desired fineness (even nanosized) with the shortest possible grinding time.

The powder obtained in the manner described above were characterized by X-ray diffraction (XRD) employing Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). The diameters of the particles in the milled powder were measured by using the laser-scattering particle-size distribution analyzer. The specific surface area of the milled powders was evaluated by using a BET analyzer (Yuasa Ionics, Autosorb 6AG). All the milled powders were characterized by using a scanning electron microscope (SEM).

2.3 Catalytic activity tests

A thermogravimetric analyzer (TGA) was used to examine the catalytic activity of LFO for soot oxidation. Samples were thoroughly mixed with a mass ratio of an LFO and reference soot = 9: 1, in which powder of carbon black (Printex[®] V, Degussa) with average size of 25 μm was used as the reference soot. The powder obtained in the manner described above was mixed again in ethanol (under wet conditions) for 5 min using an ultrasonic homogenizer and then desiccated. Subsequently, 7 mg of the desiccated samples was analyzed in a TGA. The samples were heated to 700 $^{\circ}\text{C}$ at a rate of 3 $^{\circ}\text{C}/\text{min}$ and an air-flow rate of 50 ml/min. In the resulting mass loss curve obtained, T_{50} was defined as the temperature at which the weight of the reference soot decreased to half its initial weight. Pt/ Al_2O_3 (JRC-PTAL-1; Pt: 1 mass% from Nikki-Universal Co. Ltd.) was also used as a reference for evaluating the catalytic activity of LFO for soot oxidation.

3. Results and discussion

3.1. Characteristics of milled/unmilled LFO obtained by SHS

Fig. 2 shows the XRD patterns of the LFO samples obtained by SHS as well as those of unmilled LFO samples and LFO samples milled in the inclined planetary mill for different periods of time. The XRD patterns of the raw materials are given for reference. The raw materials mixture was ground in a ball mill for 3 h prior to SHS was performed. As expected, the product was obtained in the form of perovskite; the formation of perovskite (LFO) was confirmed from the peaks in **Fig. 2**. Additionally, it was found that as the milling time increased, the intensity of the peaks decreased and peak broadening occurred. This is probably because the degree of crystallinity of the product decreased with a decrease in the particle diameter.

Fig.3 shows crystal size of the products milled at different times, in which crystal size of the product can be evaluated by Scherrer's equation:

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

Where, D; thickness of crystallite, K; constant dependent on crystallite shape (0.9), λ ; X-ray wavelength, β = FWHM (full width at half max) or integral breadth, θ ; Bragg Angle. The size of the products decreased with milling time, as expected, reaching 21.1 nm at 6 hours.

Fig.4 shows the values of the average particle diameter at different milling times. Interestingly, the average particle diameter of the LFO samples ranged from 12 μm to 0.82 μm ; the former is the average particle diameter of unmilled LFO and the latter is that of the LFO sample milled for 0.5 h. Moreover, the diameter decreased further to a minimum of 0.34 μm as the milling time was increased to 4 h then increased to 0.73 μm after 6 h of milling. This increase was caused by the agglomeration of the fine powders of the product. Therefore, the average particle diameter at a milling time of 4 h is considered to be the lowest particle size attainable by milling. On the basis of the obtained results, we assumed that the particle size changes most significantly within the first 0.5 h of milling under the milling conditions used in our experiments.

Fig.5 shows the SEM images of the milled/unmilled LFO obtained by SHS. This figure shows that the unmilled LFO powder contains nonagglomerated particles with sizes in the range of 1–15 μm . The SEM images also show that the LFO powder milled for 6 h contains agglomerated particles with sizes in the range of 0.2–8 μm . This is due to an increase in the factors that cause adherence between particles, such as moisture, static electricity, and intermolecular force. These results clearly indicate the reason for the particle diameter reaching a minimum value after 4 h of milling, as shown in the plot

in **Fig.4**. Such agglomeration of particles was partially observed in SEM images of 2h sample and 4h one, together with a decrease in the particle size.

Fig.6 shows the BET surface area of the LFO obtained by SHS. The unmilled sample had a particularly small specific surface area ($0.89 \text{ m}^2/\text{g}$). This could be explained by the fact that generally, the BET surface area of perovskite obtained by conventional methods is $1\text{--}10 \text{ m}^2/\text{g}$ [12]. While the BET surface area of the unmilled LFO was $0.89 \text{ m}^2/\text{g}$, that of the LFO sample milled for 4 h was $48 \text{ m}^2/\text{g}$. For milling times greater than 4 h, the BET surface area of the milled LFO sample remained constant or decreased slightly because of the formation of dense agglomerates.

3.2. Catalytic activity of milled/unmilled LFO obtained by SHS

Fig.7 shows the oxidative activity of LFO. The figure shows that T_{50} decreases as the milling time increases. T_{50} was approximately 485 °C before milling and decreased to 429 °C after only 0.5 h of milling and then to 404 °C after 6 h of milling. The value of T_{50} after 6 h of milling (404 °C) was approximately 70 °C lower than that of Pt/Al₂O₃ (471 °C) and approximately 80 °C lower than that of unmilled LFO, 485 °C. The experiments were several times repeated to confirm the reproducibility with accuracy of $\pm 1^\circ\text{C}$. Macroscopically, it is reasonable that the catalytic activity for soot oxidation improved with an increase in the BET surface area (see Fig.6) and decrease in the average particle size (see Fig.4), because of an increase in the contacting area between catalyst and reference soot. Microscopically, the effect of crystal size on catalytic activity was observed. That is, smaller crystal size caused larger catalytic activity (see Fig.3), as the same as several papers reported [13-16].

The results indicate that LFO milled for 6 h shows strong catalytic activity for reference soot oxidation. The catalytic reaction on the perovskite surface proceeds at a fast rate because of the large surface area of the catalyst [17]. The catalytic activity of LFO obtained from SHS can be increased to a considerable extent ball milling. As a result, LFO obtained from SHS and milled for 6 h showed superior catalytic activity than Pt/Al₂O₃ catalyst for soot oxidation.

In conclusions, MA improved the oxidative activity of SHS-derived LFO for reference soot oxidation. 1) The diameter of the particles decreased drastically with an increase in the milling time. 2) The BET surface area increased to as much as 48 m²/g after milling for 4 h; for milling times greater than 4 h, it remained almost constant. 3) The values of T_{50} after 2 h and 6 h of milling were almost identical (404 °C); this was the minimum value of T_{50} . These trends suggest that the BET surface area of LFO subjected to MA increased with the milling time; as a result, T_{50} decreases. These results also suggest that LFO might be a suitable alternative to Pt/Al₂O₃ for oxidation of diesel particulate matter, without doping. Also, the combination of SHS and MA has a new possibility to design new catalyst.

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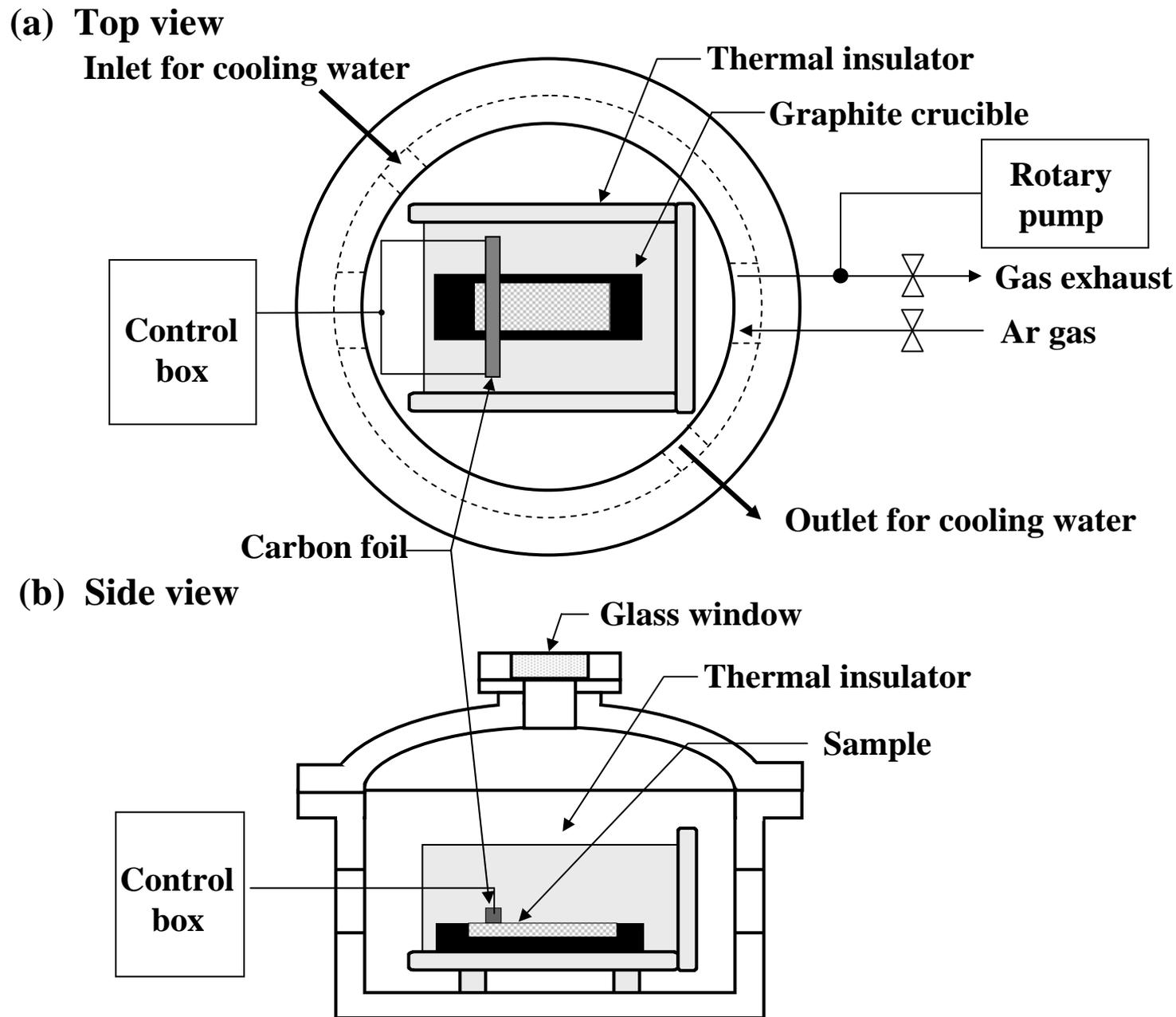


Fig. 1. Schematic diagram of the experimental apparatus used for the preparation of catalysts by SHS.

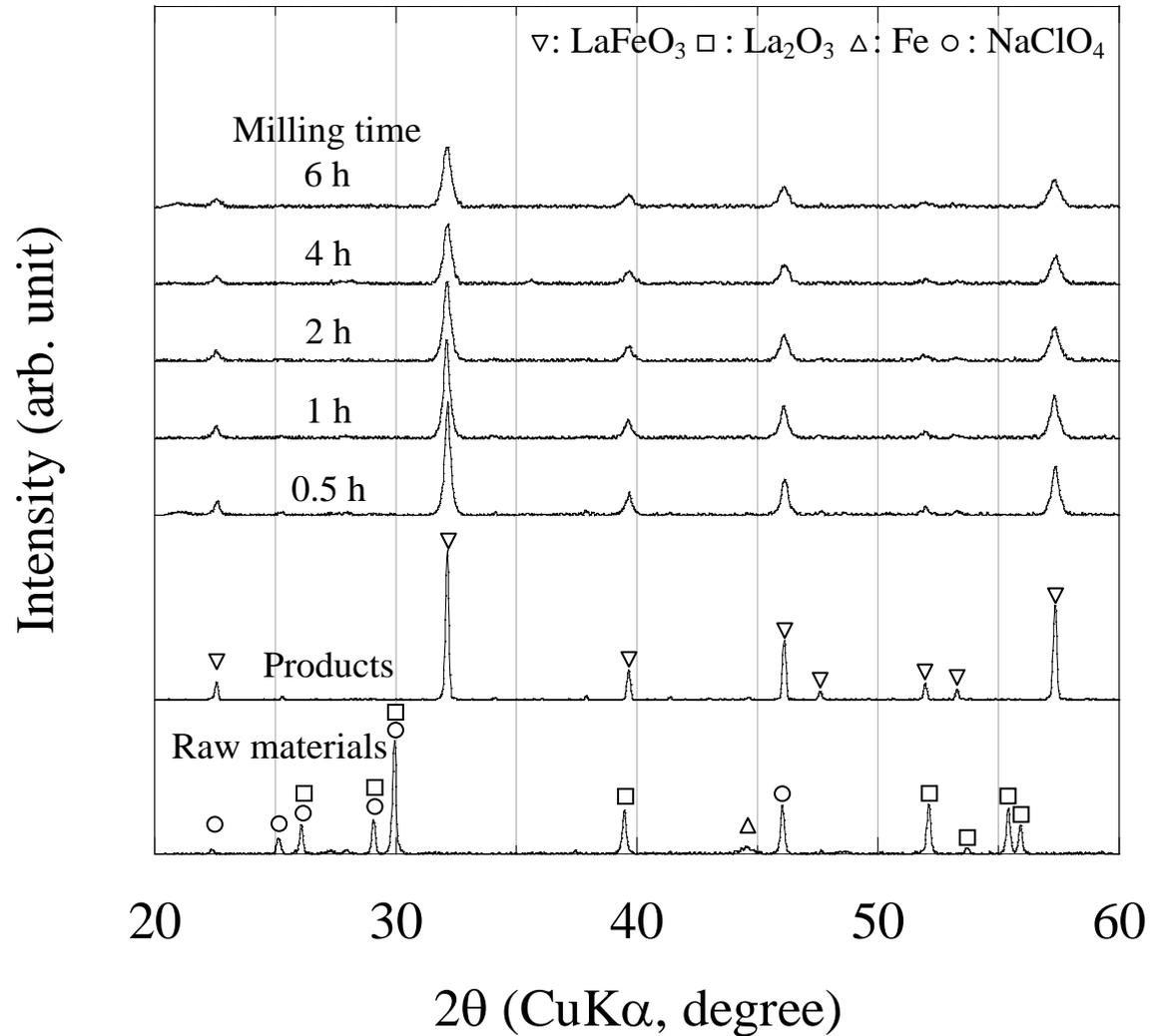


Fig. 2. XRD patterns of the raw materials, those of the products of SHS (LFO), and those of LFO milled at different periods in the inclined planetary ball mill.

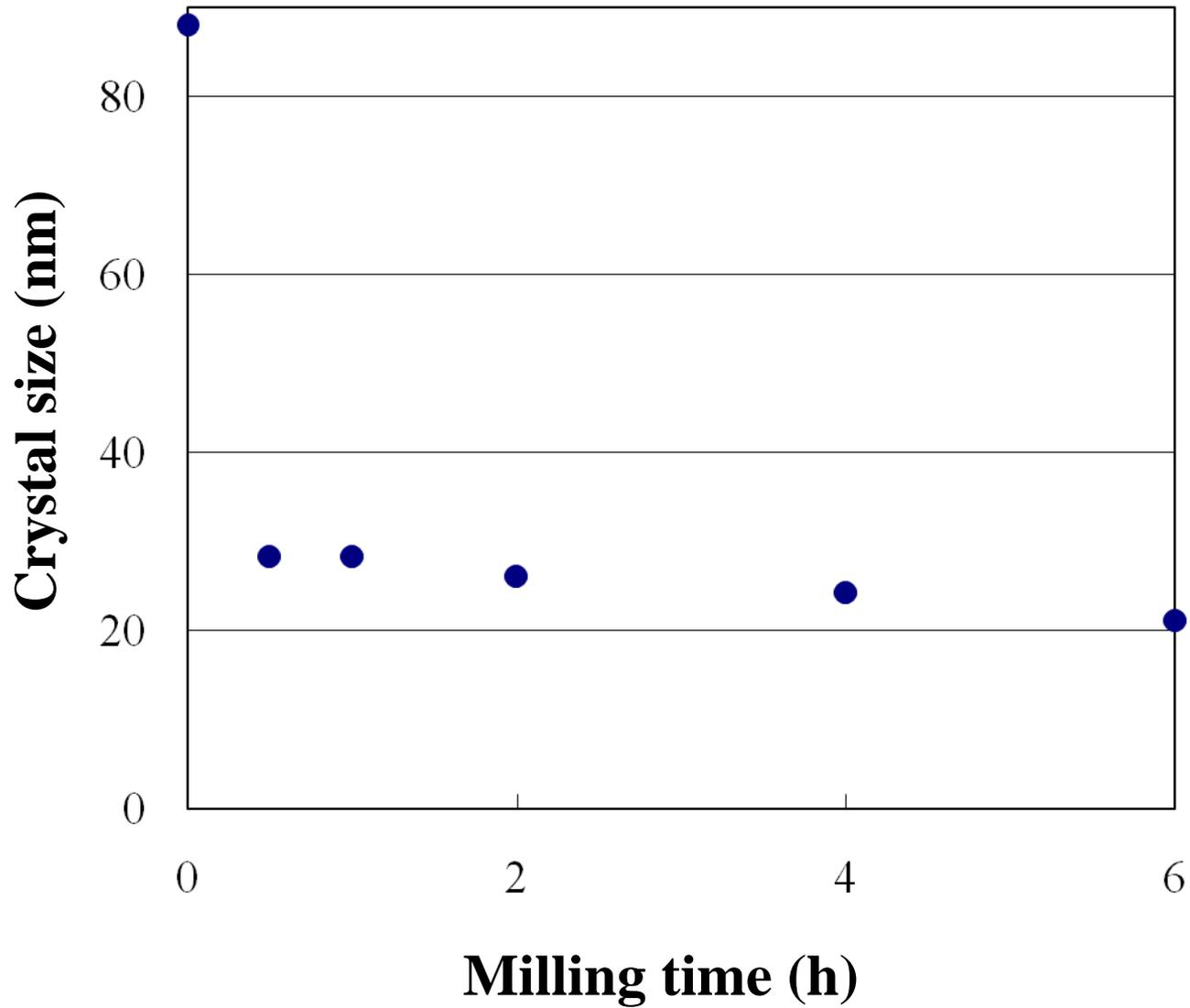


Fig. 3. Crystal size of LFO particles milled using the inclined planetary mill for different periods of time.

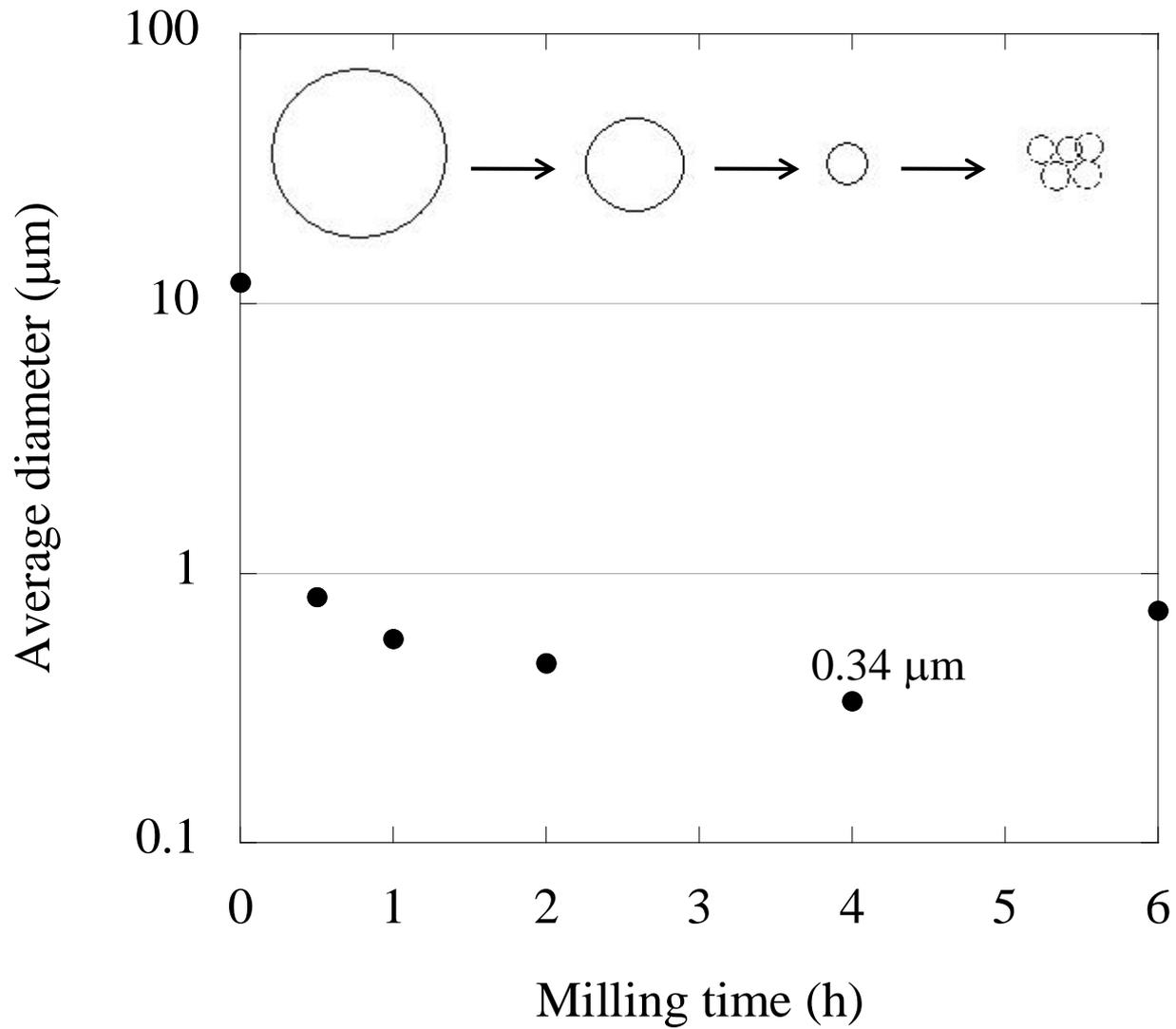


Fig. 4 Average diameter of LFO particles milled using the inclined planetary mill for different periods of time.

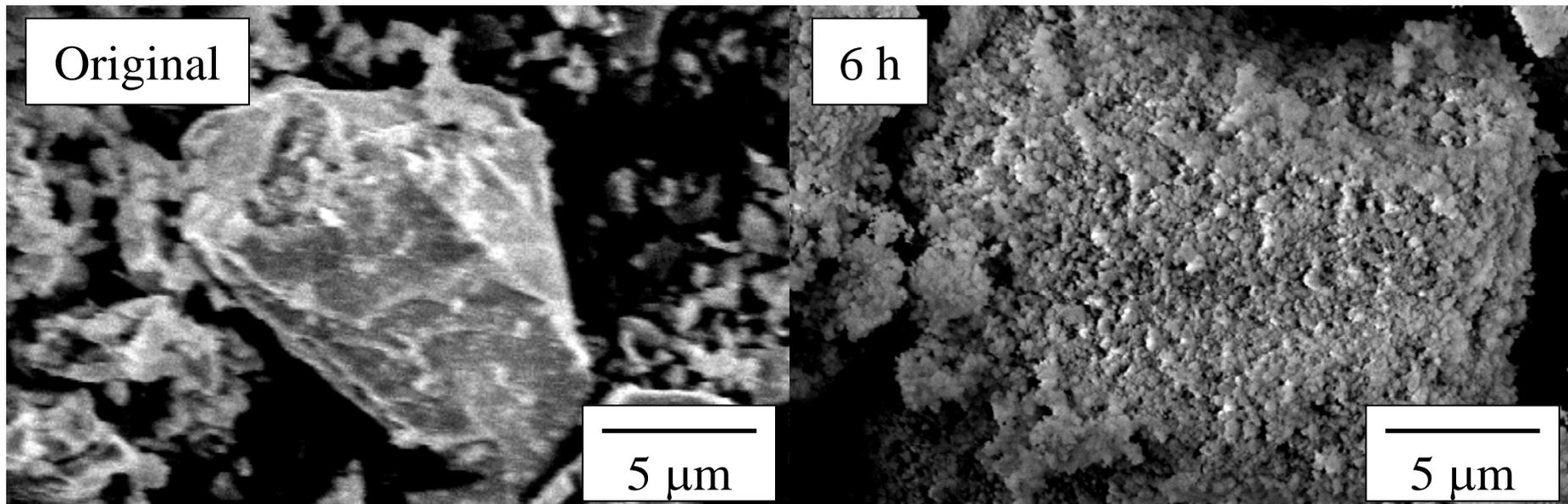


Fig. 5 SEM images of unmilled LFO and milled LFO.

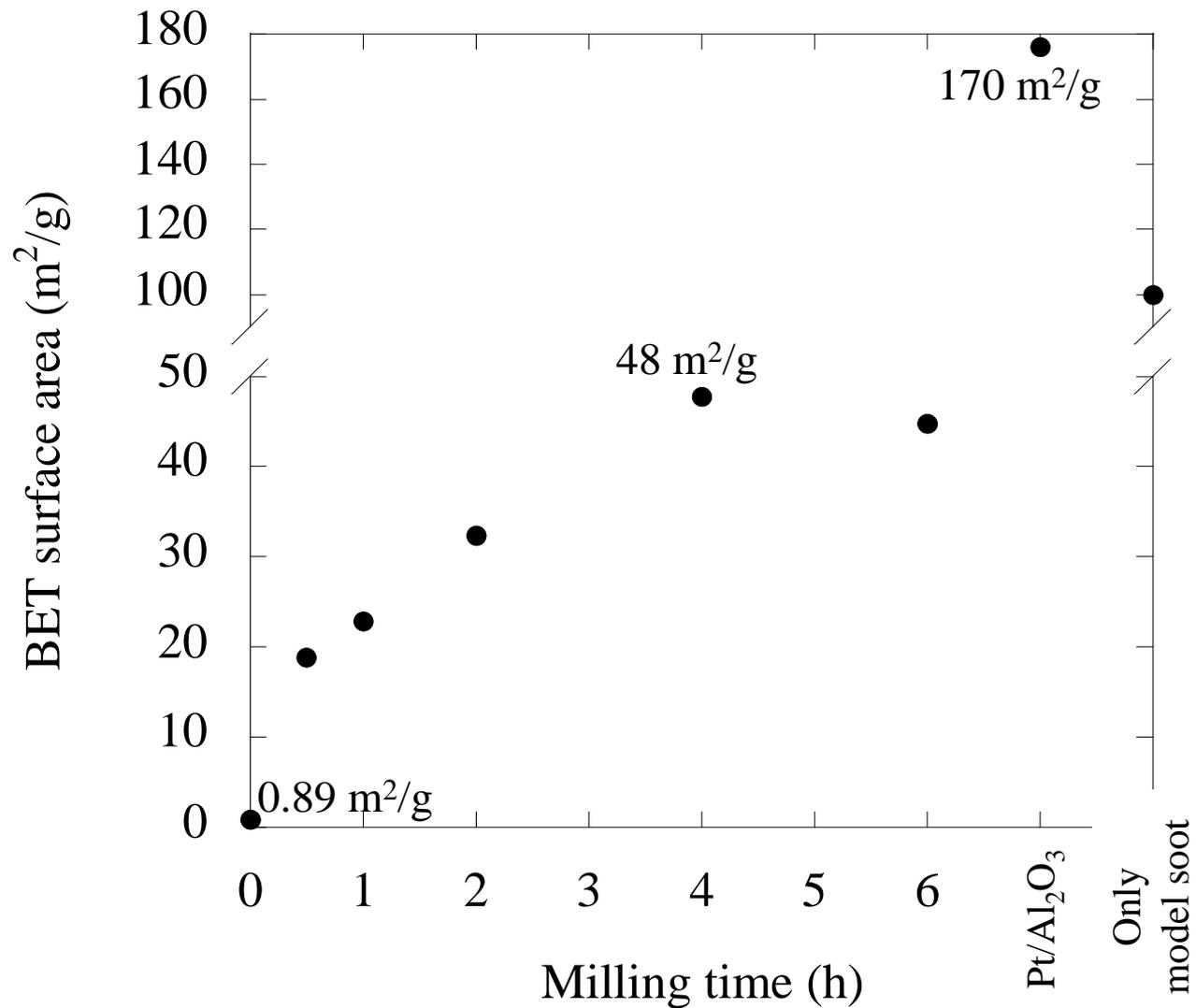


Fig. 6 BET surface area of the LFO samples obtained from SHS and milled for different periods of time in the inclined planetary mill.

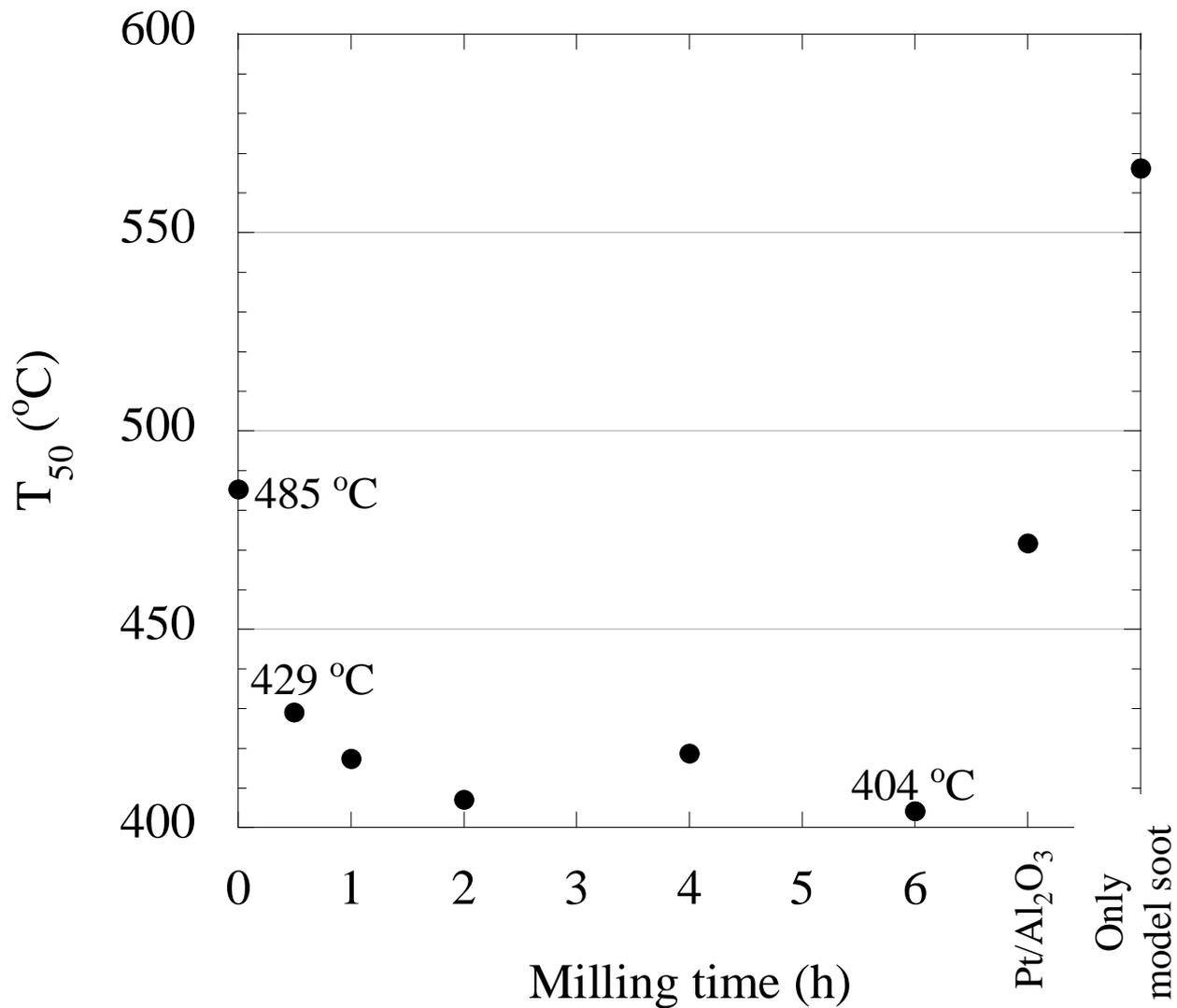


Fig. 7 Values of T_{50} of the model soot (i) in the presence of LFO milled for different periods of time, (ii) in the presence of Pt/Al₂O₃ (Pt: 1 mass%), and (iii) in the absence of a catalyst.