

Characterization and Catalytic Properties of Surface La-rich LaFeO₃ Perovskite

Young-Gil Cho, Kyong-Hoon Choi,[†] Yong-Rok Kim,[†] Jin-Seung Jung,[‡] and Sung-Han Lee*

*Department of Chemistry, Yonsei University, Wonju 220-710, Korea. *E-mail: shl2238@yonsei.ac.kr*

[†]*Department of Chemistry, Yonsei University, Seoul 120-749, Korea*

[‡]*Department of Chemistry, Kangnung National University, Gangnung 210-320, Korea*

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Perovskite-type LaBO₃ (B = transition metal) oxides are proved to be highly active catalysts for oxidation reactions in connection with air pollution control. Especially, they are considered as potential catalysts in substitution of noble metal catalysts because of their high thermostability. Many investigators have suggested that oxygen vacancies in the perovskite oxides play a major role in catalytic oxidations although there is still debate on the origin of their catalytic activity.¹⁻⁷ In LaBO₃ perovskite, oxygen vacancies can be generated by a partial substitution of the lanthanum ion or transition metal ion with an element of different valence, or by altering the La/B ratio in the preparation.⁸ To obtain a homogeneous and single phase LaBO₃ perovskite, the sol-gel method or the co-precipitation method is usually used. However, a part of transition metal atoms in LaBO₃ perovskite can exist in higher or lower oxidation states, which may induce the formation of anion or cation defects in the oxide. Accordingly, the surface composition may be different from the bulk one, which may significantly modify the catalytic properties of pure LaBO₃ perovskite.

LaFeO₃ perovskite catalyst is known to be highly active in total oxidation of methane. Its activity is generally explained by the fluctuation between two stable oxidation states of Fe, Fe²⁺ and Fe³⁺, where surface oxygen species are partly consumed and regenerated during a continuous cycle.⁷ However, the iron atoms at the B site may be present in higher oxidation state as suggested by several investigators.^{2,9} If some Fe⁴⁺ ions exist in LaFeO₃, some lanthanum ions could be removed from the lattice, based on the principle of controlled valency. The lanthanum oxide liberated from the LaFeO₃ perovskite structure may change the catalytic properties of the perovskite catalyst. In the previous paper,¹⁰ LaFeO₃ and LaCoO₃ prepared by the citrate sol-gel method revealed some activities in the oxidative coupling of methane above 650 °C and the activities were suggested to be attributable to lanthanum oxide unincorporated into the perovskite lattice. La₂O₃ catalyst is strongly basic and efficiently generates methyl radicals in the oxidative coupling of methane.^{11,12} If a small amount of lanthanum oxide is isolated from the LaFeO₃ perovskite lattice due to the presence of some Fe⁴⁺ ions, the perovskite catalyst would produce some C₂ hydrocarbons in the oxidative coupling of methane. The aim of this work is to find the lanthanum oxide liberated from the LaFeO₃ perovskite structure and to investigate its catalytic behaviors in CH₄/O₂ reaction above 600 °C. To do this, LaFeO₃ and La_{0.9}FeO₃ perovskite oxides were

prepared by the citrate sol-gel method and were examined as catalysts for methane oxidation at a CH₄/O₂ ratio of 5 in the temperature range of 600-800 °C at atmospheric pressure. They were characterized by BET surface area measurement, XRD, DSC, EDX, FT-IR, and XPS.

Experimental

LaFeO₃ oxides with La/Fe atomic ratios of 0.9 and 1 were prepared from lanthanum nitrate (La(NO₃)₃·6H₂O, Aldrich, > 99.99%) and ferric nitrate (Fe(NO₃)₃·9H₂O, Aldrich, > 99.99%). Both the lanthanum nitrate and iron nitrate were weighed to obtain the desired atomic ratio of La/Fe, and were then dissolved in deionized water. The resulting solution was mixed with an aqueous solution of citric acid to have the same amount of equivalents. Water was evaporated from the mixed solution at 70 °C under vacuum to produce a viscous gel. The viscous gel was incubated at 120 °C overnight to produce a solid amorphous mixture. The resulting mixture was ground, heated to 400 °C for 8 h, further heated at 800 °C for 3 h, and then cooled to room temperature at a cooling rate of 60 °C/h. The La₂O₃ sample was prepared by decomposition of lanthanum

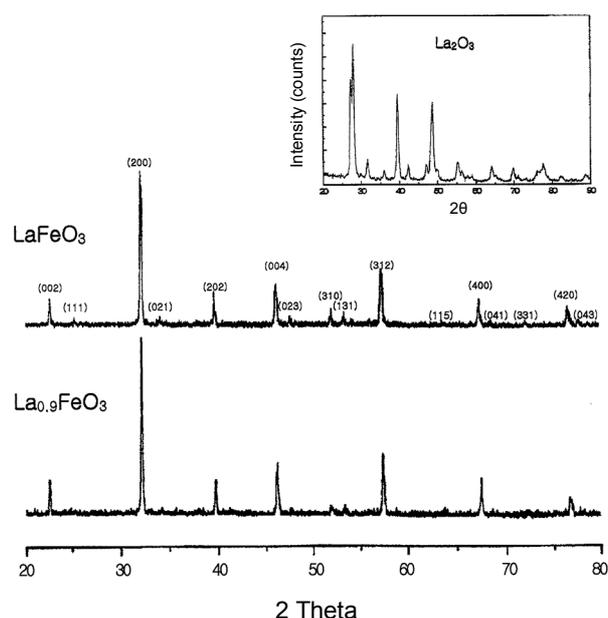


Figure 1. X-ray diffraction patterns of LaFe_{0.9}O₃, LaFeO₃, and La₂O₃ samples. La₂O₃ (JCPDS no. 24-0554); LaFeO₃ (JCPDS no. 15-0148).

nitrate at 600 °C and calcination at 800 °C in air. The BET surface areas of the samples were determined by N₂ adsorption at the temperature of liquid nitrogen using a Micromeritics Accusorb 2100 system and the values were 5.3 m²/g for the LaFeO₃ and 4.2 m²/g for the La_{0.9}FeO₃ sample. X-ray powder diffraction (XRD) analysis was performed at room temperature by using a Philips PW-1710 diffractometer with Cu-K_α radiation. A differential scanning calorimetry (DSC) analysis was carried out by a Shimadzu DSC 60 equipment in flowing dried air (10 cm³/min) at a heating rate of 10 °C/min up to 600 °C. The DSC curves of the LaFeO₃ and La_{0.9}FeO₃ samples after exposure to wet air for 72 h at room temperature are presented in Figure 2, in which the La_{0.9}FeO₃ sample shows no endotherm peaks while the LaFeO₃ sample shows a weak endotherm peak at 320 °C. To measure the bulk composition, EDX (energy dispersive X-ray) analysis was performed for the catalysts by a Genesis EDX32. The concentrations of La and Fe were determined from their K-lines and the X-ray yields were adjusted by the ZAF correction. The La/Fe atomic ratios determined by EDX were 1.05 for the LaFeO₃ and 0.94 for the La_{0.9}FeO₃ sample, indicating that the values are close to the nominal ones. The surface composition and the valence state of each element were investigated by X-ray photoelectron spectroscopy (XPS). XPS analysis of the catalysts was performed by a Kratos Axis-Nova photoelectron spectrometer unit with a monochromated Al K_α source. The base pressure in the analyzer chamber was less than 5.0 × 10⁻⁹ Torr. The resulting binding energy values were corrected using the C(1s) peak at 285.0 eV. The surface composition was calculated from the XPS peak area of each element by using the atomic sensitivity factors provided by the manufacturer. The surface La/Fe ratios determined by XPS were 1.18 for the LaFeO₃ and 1.06 for the La_{0.9}FeO₃. FT-IR spectra were obtained with a Fourier transform infrared (FT-IR) spectrometer (Perkin-Elmer Co.) at a resolution of 4.0 cm⁻¹ and 32 scans. The sample disk for the FT-IR spectroscopic analysis was made by compressing the mixture of sample (10%) and KBr. The FT-IR spectra of LaFeO₃, La_{0.9}FeO₃, and La₂O₃ samples after exposure to wet air for 72 h at room temperature. As presented in Figure 3, the La_{0.9}FeO₃ sample showed no

significant bands, while the LaFeO₃ sample showed main bands or shoulders in the range of 2000-500 cm⁻¹. The band at 1640 cm⁻¹ is ascribed to an O-H bending mode of hydroxide phase, the band at 640 cm⁻¹ is characteristic of a bending OH vibration of the lanthanum hydroxide phase, and the bands at 1080 and 850 cm⁻¹ are due to the carbonates.¹³⁻¹⁶

Catalytic reaction was carried out in a continuous flow tubular reactor which consisted of a 0.8-cm-i.d. and 3-cm-long quartz tube sealed to 0.4-cm-i.d. quartz tubes on two ends. The catalyst bed was placed in the 0.8 cm-i.d. portion which was placed in a electrical furnace. To control the reaction temperature, a K-type thermocouple was placed in contact with the outside wall of the reactor next to the catalyst bed. The amount of catalyst was typically 50 mg. The catalyst loaded in the reactor was pre-treated in a flow of air (20 cm³/min) at 800 °C for 3 h. The feed flow rate of the reaction mixture at ambient condition was CH₄/O₂/He = 10/2/28 cm³/min and the flows of the gases were controlled by electronic mass flow controllers (Kofloc 3660). The purity of the gases was greater than 99.99% and the gases were dehydrated and purified with suitable filters. The gas products were analyzed by on-line gas chromatography (HP model 5890 plus) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). A cold trap was placed at the reactor exit to remove water vapor from the gaseous mixture. The conversion of methane was calculated from the amounts of products and the methane introduced into the feed stream. The selectivities were calculated on the basis of the conversion of methane to each product. The methane conversion and product selectivities were typically compared after 1 h time-on-stream.

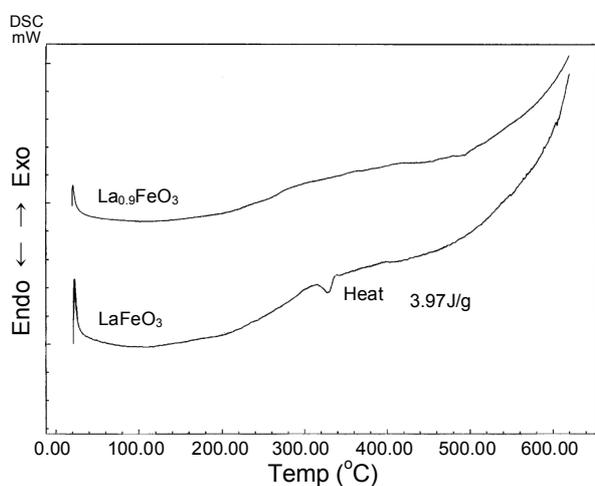


Figure 2. DSC curves of La_{0.9}FeO₃ and LaFeO₃ samples after exposure to wet air.

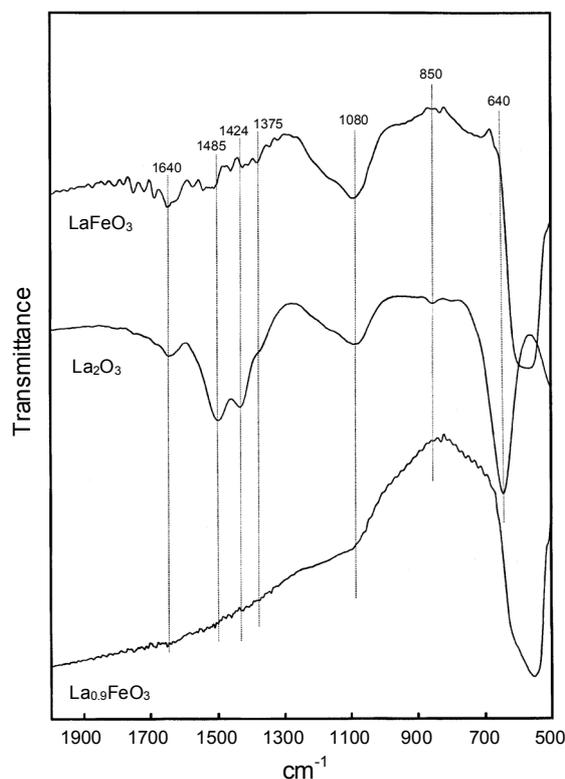


Figure 3. FT-IR spectra of La₂O₃, La_{0.9}FeO₃, and LaFeO₃ samples after exposure to wet air.

The blank tests performed in a flow of the $\text{CH}_4/\text{O}_2/\text{He}$ ($= 10/2/28$ cc/min) reaction mixture showed methane conversion of 0–2.6% to C_2 hydrocarbons in the temperature range of 600–800 °C. The details of catalytic experiment were described in the previous paper.^{17,18}

Results and Discussion

Figure 1 shows the X-ray powder diffraction patterns of the LaFeO_3 and $\text{La}_{0.9}\text{FeO}_3$ samples, which indicates the formation of monophasic perovskite oxides having orthorhombic structure. In this work, the surface La/Fe atomic ratio, 1.18, determined by XPS for the LaFeO_3 sample was higher than the nominal one, indicating that lanthanum is more rich on the surface than in the bulk. To verify the presence of lanthanum oxide liberated from the perovskite lattice, DSC analysis was performed for the sample after exposure to wet air and the results are shown in Figure 2. Because lanthanum oxide is easily converted to the hydroxide form even at room temperature in air, the lanthanum oxide aged in air reveals an endotherm peak due to the dehydration.¹³ A weak endotherm peak observed at 320 °C is attributable to the removal of hydroxyl groups from lanthanum hydroxide formed by hydration of lanthanum oxide in wet air. The result implies that lanthanum oxide in a small amount exists in the oxide. Figure 3 compares the FT-IR spectra of LaFeO_3 , $\text{La}_{0.9}\text{FeO}_3$, and La_2O_3 samples after exposure to wet air at room temperature. The FT-IR spectrum of LaFeO_3 sample displays absorption bands at 1640 cm^{-1} due to an O–H bending mode of adsorbed H_2O and 640 cm^{-1} due to a bending OH vibration of the lanthanum hydroxide phase.^{13–16} The result

supports that lanthanum oxide exists in the LaFeO_3 sample. The isolated lanthanum oxide which was not detected by XRD presumably exists as nanoparticles or amorphous in the perovskite. The liberation of lanthanum oxide from the LaFeO_3 perovskite lattice is considered to be due to the unusual oxidation state of iron, Fe^{4+} , in the oxide. When a part of Fe^{3+} ions is oxidized to Fe^{4+} ions, a part of lanthanum ions would be removed from the perovskite lattice based on the principle of controlled valency. According to Ciambelli *et al.*¹⁹ and Barbero *et al.*,²⁰ the Fe^{4+} content determined from the TPR data of LaFeO_3 perovskite is 2.8% after calcination at 600 °C and 1.3% after calcination at 800 °C, indicating that the Fe^{4+} content decreases with increasing the calcination temperature. Their results are agreeable to the present results showing the presence of isolated lanthanum oxide in the LaFeO_3 sample calcined at 800 °C.

Figure 4 reveals the XPS spectra of O(1s), La(3d), and Fe(2p). The binding energies of La 3d_{5/2}, 833.5 eV for the LaFeO_3 sample and 833.8 eV for the $\text{La}_{0.9}\text{FeO}_3$ sample, correspond to La^{3+} ions in oxide form and the binding energy of Fe 2p_{3/2}, 710.2 eV for both the samples, corresponds to Fe^{3+} ions in oxide form.^{9,21} We could not distinguish Fe^{3+} and Fe^{4+} from the Fe(2p) XPS signal. The O(1s) XPS signal of $\text{La}_{0.9}\text{FeO}_3$ sample was divided into two peaks at 529.9 and 532.1 eV, while that of LaFeO_3 sample was divided into three peaks at 529.4, 531.9, and 534.4 eV. The O(1s) binding energies at 529.9 eV and 529.4 eV are ascribed to lattice oxygen species. The binding energies at 532.1 and 531.9 eV can be assigned to chemisorbed oxygen species (O^-) or OH^- species because the O(1s) binding energy of O^- or OH^- ion is generally higher by

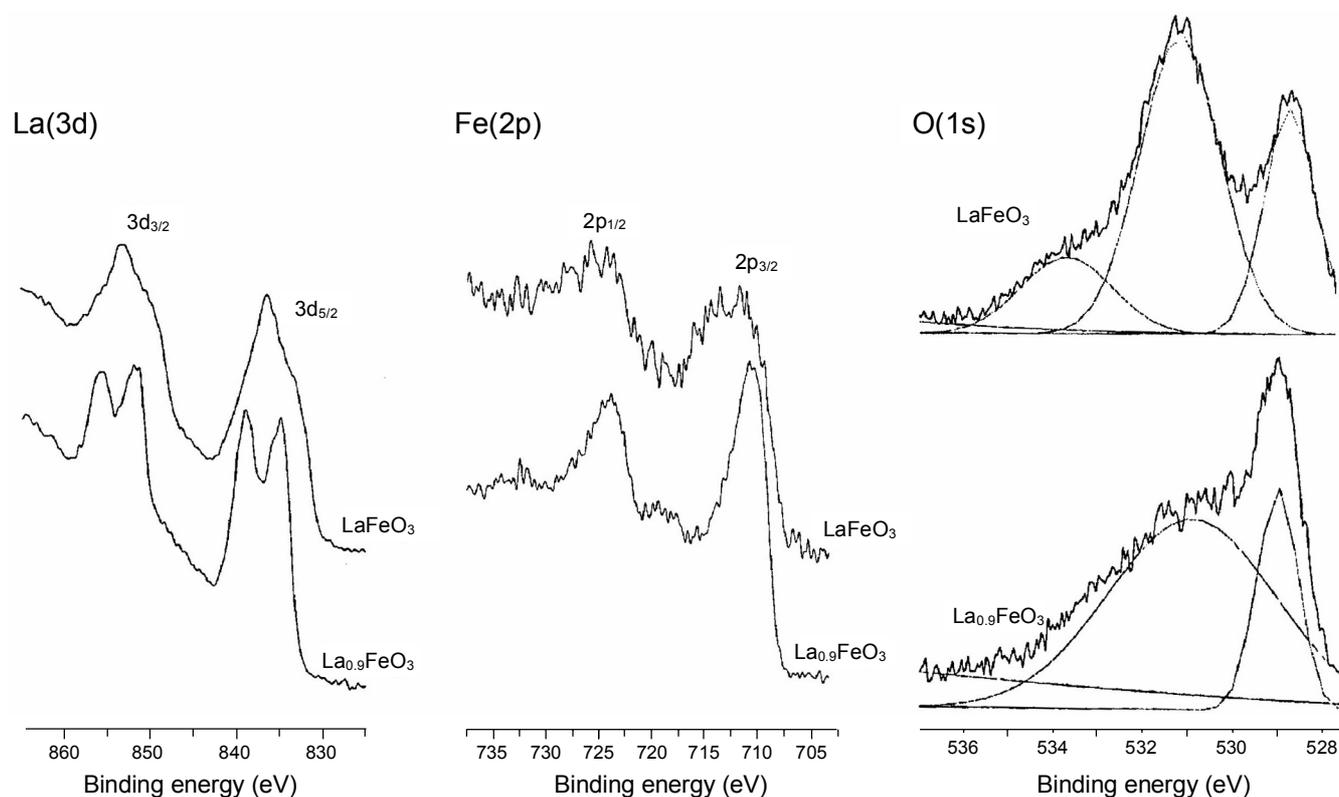


Figure 4. La(3d), Fe(2p), and O(1s) XPS spectra of $\text{La}_{0.9}\text{FeO}_3$ and LaFeO_3 samples.

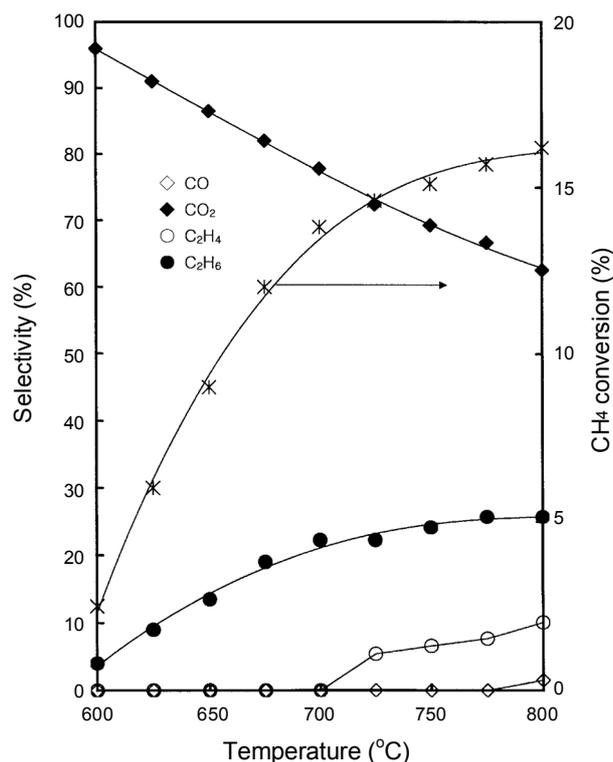


Figure 5. Selectivities and methane conversion of LaFeO₃ catalyst for methane oxidation at a CH₄/O₂ ratio of 5 in the temperature range of 600-800 °C.

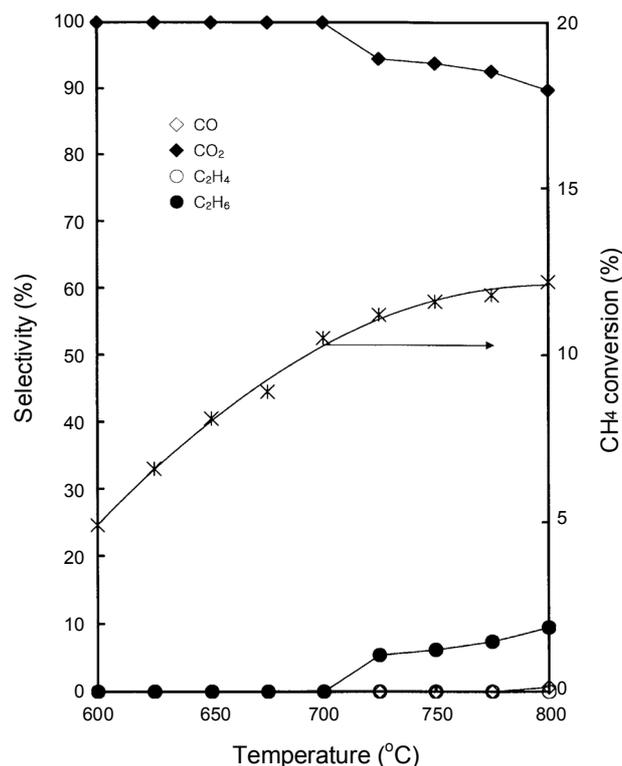


Figure 6. Selectivities and methane conversion of La_{0.9}FeO₃ catalyst for methane oxidation at a CH₄/O₂ ratio of 5 in the temperature range of 600-800 °C.

a 2.1-2.5 eV than that of lattice oxygen.²² The binding energy at 534.4 eV observed for the LaFeO₃ sample is attributed to the adsorbed water species.²² Because lanthanum oxide is easily hygroscopic when it is exposed to air, the higher O(1s) binding energy (534.4 eV) is considered to be due to water molecule associated with the surface lanthanum oxide.

In the CH₄/O₂ reaction, the LaFeO₃ catalyst produced CO₂, C₂H₄, and C₂H₆ as major products in the temperature range of 600-800 °C. Figure 5 shows methane conversion and product selectivities of the LaFeO₃ catalyst, in which the C₂ yield at 800 °C is 5.8% in a selectivity of 35.8%. On the other hand, the La_{0.9}FeO₃ catalyst showed total oxidation activity for the reaction as shown in Figure 6. The La_{0.9}FeO₃ catalyst produced C₂ hydrocarbons in a selectivity below 9.5% in the temperature range of 725 - 800 °C and the C₂ yield at 800 °C was merely 1.2%. In the previous paper, we reported that the CH₄/O₂ reaction in a quartz flow reactor produces C₂ hydrocarbons below 800 °C in the absence of catalyst.¹⁷ In this work, the blank test showed a C₂ yield of 2.6% at 800 °C and the value is higher than 1.2% of the La_{0.9}FeO₃ catalyst, suggesting the C₂ production catalyzed by the La_{0.9}FeO₃ to be negligible. Because the specific surface areas of the LaFeO₃ and La_{0.9}FeO₃ samples, 5.3 and 4.2 m²/g, are very low and do not differ significantly, the differences in catalytic properties of both the catalysts is inferred to be closely related to their surface structures.

Many investigations for the oxidative coupling of methane over metal oxide catalyst have shown that less electrophilic oxygen species adsorbed on oxygen vacancy sites effectively generate methyl radicals which are coupled to form ethane in

the gas phase.²³ The present La_{0.9}FeO₃ catalyst was found to be a single phase perovskite having orthorhombic structure by XRD. The non-stoichiometric La_{0.9}FeO₃ oxide can be written as La_{0.9}FeO_{2.85}. If some Fe⁴⁺ ions are present in the oxide, the oxide could be written as La_{0.9}(Fe³⁺_{1-x}Fe⁴⁺_x)O_{2.85+0.5x}. High activity of the La_{0.9}FeO₃ catalyst for total oxidation of methane is believed to be closely related to oxygen vacancy as suggested by other investigators.^{3,23} Because the La_{0.9}FeO₃ catalyst negligibly produced C₂ hydrocarbons in this reaction, oxygen vacancy seems to be not directly related to the formation of C₂ hydrocarbons. As mentioned above, the LaFeO₃ sample is considered to be a mixed phase of isolated lanthanum oxide and lanthanum-deficient LaFeO₃ perovskite oxide. It can be represented as $\frac{x}{6} \text{La}_2\text{O}_3 / \text{La}_{1-\frac{x}{3}}(\text{Fe}_{1-x}^{3+}\text{Fe}_x^{4+})\text{O}_3$. The isolated lanthanum oxide may be related to the nature and reactivity of the perovskite surface. Lanthanum oxide is known to be an active and selective catalyst for the oxidative coupling of methane,^{12,23} which enables us to consider that the C₂ production over the LaFeO₃ catalyst is attributed to the surface lanthanum oxide. In the oxidative coupling of methane over metal oxide catalyst, CO is generally produced as a major product. However, the present LaFeO₃ catalyst scarcely produced CO in the reaction as shown in Figure 6, which implies that CO can be further oxidized to CO₂ on the perovskite containing oxygen vacancies which act as active site for total oxidation of methane.

Consequently, when the LaFeO₃ perovskite is prepared by the citrate sol-gel method and calcined at 800 °C, lanthanum deficiencies are created in the LaFeO₃ perovskite owing to the presence of Fe⁴⁺ ion in the perovskite, resulting in the libera-

tion of lanthanum oxide from the perovskite lattice. The LaFeO₃ perovskite catalyst shows total oxidation activity in the CH₄/O₂ reaction below 700 °C, but above 700 °C it shows some activity for the oxidative coupling of methane. The surface lanthanum oxide liberated from the perovskite structure is responsible for the modification of catalytic properties of LaFeO₃.

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