

## Catalytic Activities of Perovskite-type $\text{LaBO}_3$ ( $\text{B} = \text{Fe}, \text{Co}, \text{Ni}$ ) Oxides for Partial Oxidation of Methane

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Direct conversion of methane to  $\text{C}_2$ -hydrocarbons via oxidative coupling reaction has received a great deal of attention for the last twenty five years because the reaction has been recognized as a promising route for the production of ethylene from natural gas.<sup>1,2</sup> However, the process is considered to be economically unfeasible because the yield of ethylene produced in the reaction is less than 25%. In recent, it has been proposed that the disadvantage may be overcome by integrating with processes involving endothermic reactions such as cracking of ethane to ethylene and steam reforming of methane to synthesis gas and the heat of the exothermic coupling reaction can be alternatively used to generate electricity.<sup>3</sup>

An interesting potential application of perovskites as catalysts is their use for redox reactions. Lanthanum-transition metal perovskite oxides ( $\text{LaBO}_3$ ) are proved to be effective catalysts for the catalytic oxidations of hydrocarbons, CO, and ammonia and considered to be promising materials for application as electrode materials in solid oxide fuel cells.<sup>4-8</sup> There are few reports on the application of  $\text{LaBO}_3$  oxides to the catalytic partial oxidation of methane. Tagawa *et al.*<sup>6</sup> found that the  $\text{LaAlO}_3$  catalyst prepared by the mist decomposition method is highly active and selective for the oxidative coupling of methane and proposed that an amorphous phase of  $\text{LaAlO}_3$  is responsible for the catalytic activity. Spinicci *et al.*<sup>8</sup> found that both catalytic activity and  $\text{C}_2$ -selectivity are largely enhanced when  $\text{Al}^{3+}$  ion in the  $\text{LaAlO}_3$  perovskite is substituted with  $\text{Li}^+$  or  $\text{Mg}^{2+}$ . In the oxidative methane coupling reaction catalyzed by metal oxide, the transfer of oxygen to the surface from bulk or gas phase is very important on its catalytic activity because the abstraction of a hydrogen from methane is caused by an oxygen ion present on the surface of metal oxide catalyst.  $\text{LaBO}_3$  perovskite oxides may be suitable catalysts for the methane coupling reaction because they are characterized by high mobility of oxygen ions. Actually, the perovskite oxides have received increasing interest in the mixed-conducting ceramic membrane reactor technology for partial oxidation of methane.<sup>9</sup> In this work, we prepared  $\text{LaFeO}_3$ ,  $\text{LaCoO}_3$ , and  $\text{LaNiO}_3$  perovskite oxides by using a sol-gel method and examined them as catalysts for the oxidative coupling of methane in the temperature range of 650 to 800 °C at atmospheric pressure.

### Experimental Section

$\text{La}_2\text{O}_3$  catalyst was prepared by decomposition of lanthanum nitrate ( $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , Aldrich, > 99.9%) in air at 500 °C, grinding of the powder, and calcination in air at 850 °C for 24 h.  $\text{LaBO}_3$  ( $\text{B} = \text{Fe}, \text{Co}, \text{Ni}$ ) catalysts were prepared from citrate precursors. Both the lanthanum nitrate and transition metal nitrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , Aldrich, > 99.9%) were weighed to yield the metal atomic ratio of  $\text{La} : \text{B} = 1 : 1$  and dissolved in deionized water. The resulting solution was mixed with an aqueous solution of citric acid by fixing at unity of the molar ratio of citric acid to the metal ions. Water was evaporated from the mixed solution at 70 °C in vacuum until a viscous gel was obtained. The mixture was kept at 100 °C overnight, ground and finally calcined at 850 °C for 24 h. X-ray powder diffraction analysis was performed for the catalysts using a Philips PW-1710 diffractometer with Ni-filtered  $\text{Cu K}\alpha$  radiation. The JCPDS powder diffraction file was used to identify the crystalline phases present. BET surface areas were measured by nitrogen adsorption at -196 °C with a Quantichrome automatic gas adsorption system. Thermogravimetric (TG) and differential scanning calorimetry (DSC) analyses were performed using a TA Instrument in flowing air (10  $\text{cm}^3/\text{min}$ ) with a heating rate of 10 °C/min up to 600 °C.

Catalytic tests were carried out in a continuous flow tubular quartz reactor, 0.8 cm i.d., employing 200 mg of catalyst. The feed flow rate of reaction mixture at ambient condition was  $\text{CH}_4/\text{O}_2/\text{He} = 8/2/10 \text{ cm}^3/\text{min}$ . The reaction was investigated in the temperature range of 650-800 °C after *in situ* pre-treatment of the catalysts in a flow of  $\text{O}_2(20\%)/\text{He}$  mixture at 800 °C for 1 h. The details of kinetic measurements are described in the previous paper.<sup>2</sup> To get an information about the chemical species adsorbed on the catalyst surface, FT-IR (Fourier-transform infrared) spectroscopy analysis was performed by using an infrared cell as described in the literature.<sup>10</sup> The IR cell was made of quartz tubing with 10 cm length and 3.0 cm diameter, heating coil was wound around the middle of the cell to control the reaction temperature, two turns of copper cooling coils were placed around each end of the cell, and Zn-Se windows were attached to both ends of the cell. For the

*in situ* IR spectroscopy analysis, the self-supported disk of LaFeO<sub>3</sub> was made by compressing the powder (50 mg) at 3 t/cm<sup>2</sup> and the La<sub>2</sub>O<sub>3</sub> disk was made by compressing the mixture of La<sub>2</sub>O<sub>3</sub>(10%) and KBr. The catalyst disk was mounted in a quartz holder within the IR cell connecting to the gas handling system and the CH<sub>4</sub>/O<sub>2</sub>/He reaction mixture was admitted into the IR cell at 650 °C. After the reaction for 1 h, the IR cell was rapidly cooled to 25 °C and then the IR spectrum was obtained by using FT-IR spectrometer (JASCO 300E) with a resolution of 4.0 cm<sup>-1</sup> and 64 scans.

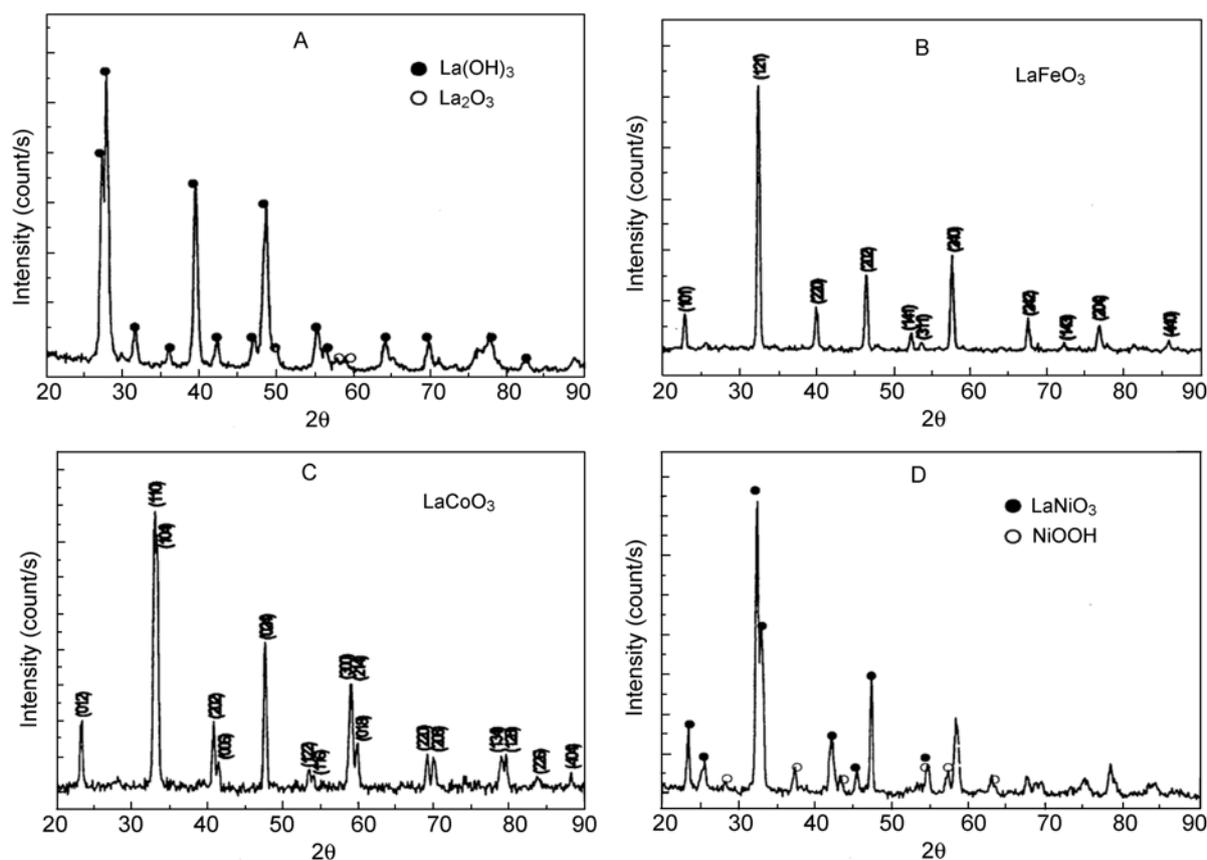
## Results and Discussion

The catalysts prepared in this work showed catalytic

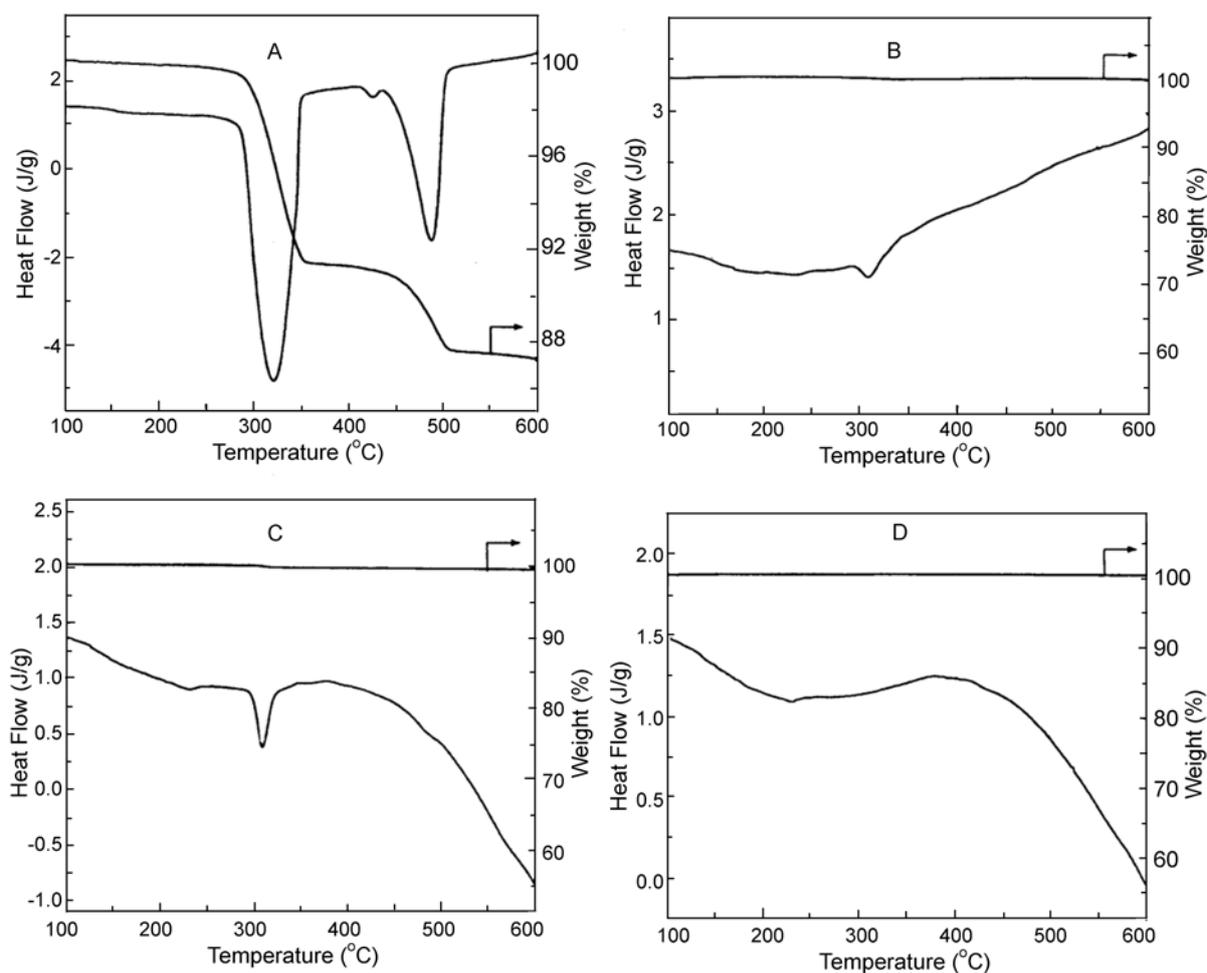
activity for the oxidative coupling of methane and major products were H<sub>2</sub>, CO, CO<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, and C<sub>3</sub> hydrocarbons in the temperature range of 650-800 °C. Table 1 shows the methane conversion and product selectivities of catalysts when the reaction mixture was fed over the catalysts at atmospheric pressure. Among the catalysts tested in this work, the LaFeO<sub>3</sub> catalyst showed the best C<sub>2</sub>-yield of 12.0% with a selectivity of 53.2% at 750 °C, which is rather appreciable. Figure 3 exhibits variation of methane conversion with reaction temperature in the range of 650-800 °C and Figure 4 exhibits variations of C<sub>2</sub>-selectivity with reaction temperature, in which the perovskite catalysts show higher CH<sub>4</sub> conversion and C<sub>2</sub>-selectivity than the La<sub>2</sub>O<sub>3</sub> catalyst. In the temperature range of 650-800 °C, C<sub>2</sub>-yield is 0.9-4.8% for the La<sub>2</sub>O<sub>3</sub> catalyst, 5.4-12.0% for the LaFeO<sub>3</sub>

**Table 1.** Methane conversion and product selectivity for oxidative coupling of methane over LaBO<sub>3</sub> catalysts

Catalyst	BET surface area (m <sup>2</sup> /g)	T (°C)	Methane conversion (%)	Selectivity (%)						C <sub>2</sub> yield
				H <sub>2</sub>	CO	CO <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> <sup>-</sup>	
La <sub>2</sub> O <sub>3</sub>	5.968	750	16.3	2.1	14.3	53.1	13.3	15.9	1.3	4.8
La <sub>3</sub> FeO <sub>3</sub>	3.160	750	22.5	0.5	5.6	38.2	26.2	27.0	2.5	12.0
LaCoO <sub>3</sub>	2.840	750	23.2	1.0	3.6	45.5	21.7	26.8	1.4	11.3
LaNiO <sub>3</sub>	2.697	700	22.3	1.9	6.5	48.9	19.9	22.7	0.1	9.5



**Figure 1.** X-ray diffraction patterns of (A) La<sub>2</sub>O<sub>3</sub>, (B) LaFeO<sub>3</sub>, (C) LaCoO<sub>3</sub>, and (D) LaNiO<sub>3</sub> catalysts aged in air. La(OH)<sub>3</sub> (JCPDS no. 36-1481); La<sub>2</sub>O<sub>3</sub> (JCPDS no. 40-1284); LaFeO<sub>3</sub> (JCPDS no. 37-1493); LaCoO<sub>3</sub> (JCPDS no. 25-1060); LaNiO<sub>3</sub> (JCPDS no. 12-0751); NiOOH (JCPDS no. 27-0956).



**Figure 2.** TG and DSC curves of (A)  $\text{La}_2\text{O}_3$ , (B)  $\text{LaFeO}_3$ , (C)  $\text{LaCoO}_3$ , and (D)  $\text{LaNiO}_3$  catalysts aged in air.

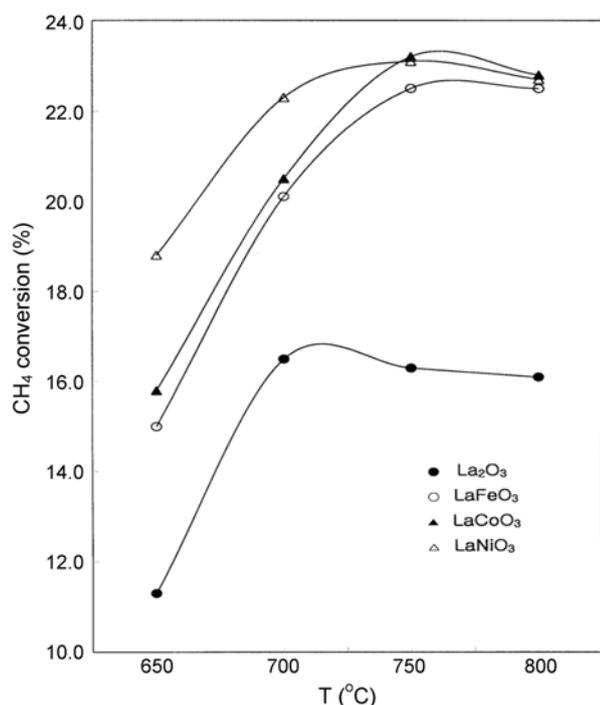
catalyst, 6.2–11.3% for the  $\text{LaCoO}_3$  catalyst, and 6.1–9.5% for the  $\text{LaNiO}_3$  catalyst.

Figure 1 presents the X-ray diffraction patterns of catalysts. The XRD result of  $\text{La}_2\text{O}_3$  catalyst aged in air shows the presence of  $\text{La}(\text{OH})_3$  as a major crystalline phase, indicating  $\text{La}_2\text{O}_3$  to be hydrated even at room temperature in air. As shown in Figure 2(A), the TG result of  $\text{La}_2\text{O}_3$  catalyst revealed the total weight loss of about 13% in the temperature range of 100–600 °C, indicating lanthanum hydroxide to be mostly dehydroxylated below 600 °C. The DSC curve of  $\text{La}_2\text{O}_3$  catalyst in Figure 2(A) shows two strong endotherm peaks at 320 °C and 490 °C. The endotherm at 320 °C is attributed to the removal of hydroxyl groups from lanthanum hydroxide and the endotherm at 490 °C is attributed to the removal of hydroxyl groups from lanthanum oxyhydroxide ( $\text{LaO}(\text{OH})$ ).<sup>11</sup> Figure 5 exhibits the IR spectra of  $\text{La}_2\text{O}_3$  catalyst after exposure to the  $\text{CH}_4/\text{O}_2/\text{He}$  reaction mixture at 25 °C and 650 °C. The group of low frequency bands in the range of 1600–1300  $\text{cm}^{-1}$  corresponds to the usual vibration range of carbonate species.<sup>12,13</sup> According to the *in situ* FT-IR study on the oxidative coupling of methane over  $\text{La}_2\text{O}_3$  catalyst by Le Van *et al.*,<sup>14</sup> the dioxomonocarbonate ( $\text{La}_2\text{O}_2\text{CO}_3$ ) is formed during the

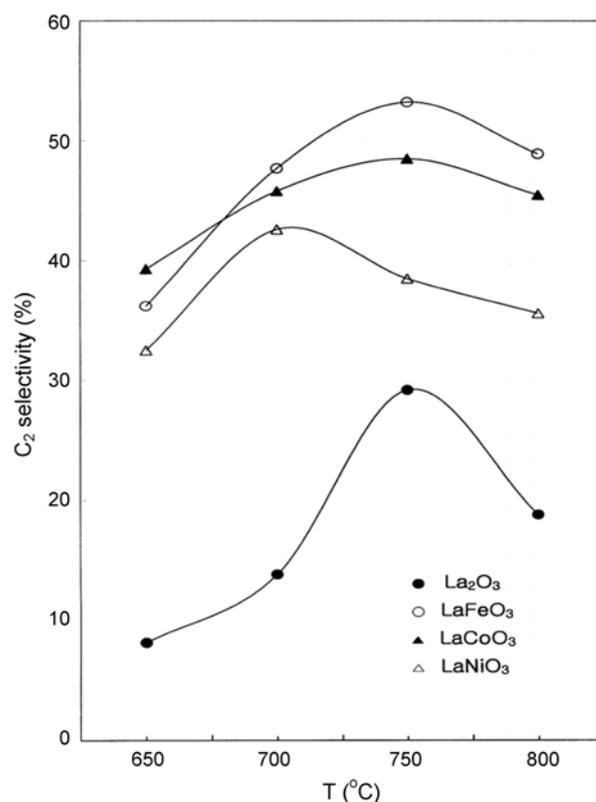
reaction at 650 °C and its IR bands appear at 1088 and 856  $\text{cm}^{-1}$ , which is in good agreement with the present result.

The X-ray diffraction pattern of  $\text{LaFeO}_3$  catalyst in Figure 1(B) shows monophasic perovskite oxide having orthorhombic structure. As shown in Figure 2(B), the DSC curve of  $\text{LaFeO}_3$  catalyst aged in air shows an endotherm peak at 310 °C and the endotherm is attributable to the removal of hydroxyl groups from lanthanum hydroxide formed by hydration of lanthanum oxide at room temperature in air. The result implies a small amount of lanthanum oxide to be isolated from the perovskite lattice during calcination at 850 °C in air and the isolated lanthanum oxide presumably exists as nanoparticles in the perovskite. Figure 6 presents the IR spectra of  $\text{LaFeO}_3$  catalyst after exposure to the  $\text{CH}_4/\text{O}_2/\text{He}$  mixture at 25 °C and 650 °C. The bands ascribing to carbonates are observed in the range of 1600–1300  $\text{cm}^{-1}$  and very weak bands ascribing to  $\text{La}_2\text{O}_2\text{CO}_3$  are observed in the range of 1100–800  $\text{cm}^{-1}$ . The IR result supports that isolated lanthanum oxide might be produced in the  $\text{LaFeO}_3$  perovskite by calcination at 850 °C in air because  $\text{La}_2\text{O}_2\text{CO}_3$  should be produced by carbonation of the surface lanthanum oxide during the catalytic reaction at 650 °C.

It may be possible that the  $\text{Fe}^{3+}$  ions in  $\text{LaFeO}_3$  perovskite

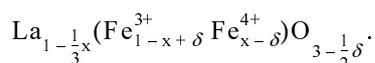


**Figure 3.** Variation of methane conversion with reaction temperature for La<sub>2</sub>O<sub>3</sub>, LaFeO<sub>3</sub>, LaCoO<sub>3</sub>, and LaNiO<sub>3</sub> catalysts.

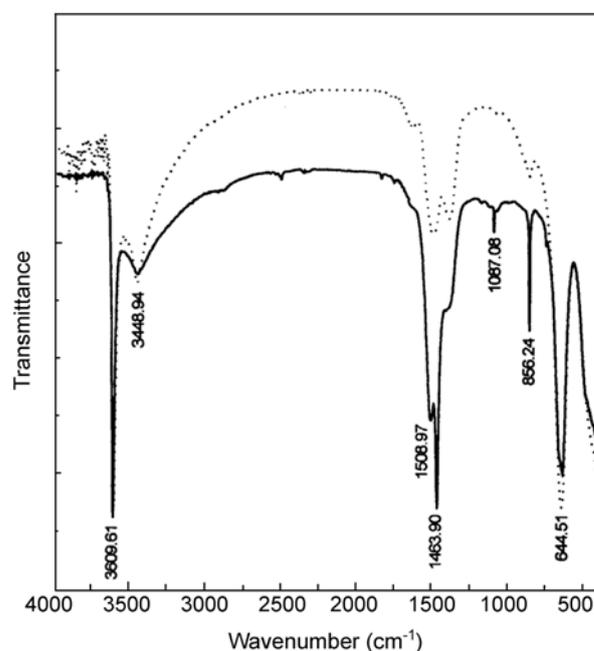


**Figure 4.** Variation of C<sub>2</sub>-selectivity with reaction temperature for La<sub>2</sub>O<sub>3</sub>, LaFeO<sub>3</sub>, LaCoO<sub>3</sub>, and LaNiO<sub>3</sub> catalysts.

are further oxidized to the Fe<sup>4+</sup> ions in the presence of gaseous oxygen at high temperatures. When a part of Fe<sup>3+</sup> ions converts to higher oxidation state (Fe<sup>4+</sup>), a part of lanthanum ions would be removed from the lattice based on the principle of controlled valency and then it can be represented as La<sub>1- $\frac{1}{3}x$</sub> (Fe<sub>1-x</sub><sup>3+</sup>Fe<sub>x</sub><sup>4+</sup>)O<sub>3</sub>. Mizusaki *et al.*<sup>15</sup> reported that lanthanum-transition metal perovskite containing an easily oxidizable transition metal cation like Fe<sup>3+</sup> shows oxygen-excess structure and p-type conductivity at atmospheric pressure and high temperatures. They suggested that since oxygen-excess composition is assumed to be possible only when the stoichiometric composition contains oxygen vacancies that can be filled by a reaction,  $\text{V}_\text{o} + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{O}_\text{o} + 2\text{h}$ , the perovskite oxide contains a small deficiency of La<sub>2</sub>O<sub>3</sub> because of the difficulty of controlling the cation ratio precisely, which is agreeable to the present result. It can be assumed that the high valency (Fe<sup>4+</sup>) of iron cations is likely to be converted to the low valency (Fe<sup>3+</sup>) since the Fe<sup>4+</sup> is unstable, which results in the formation of oxygen vacancies in the perovskite, representing as

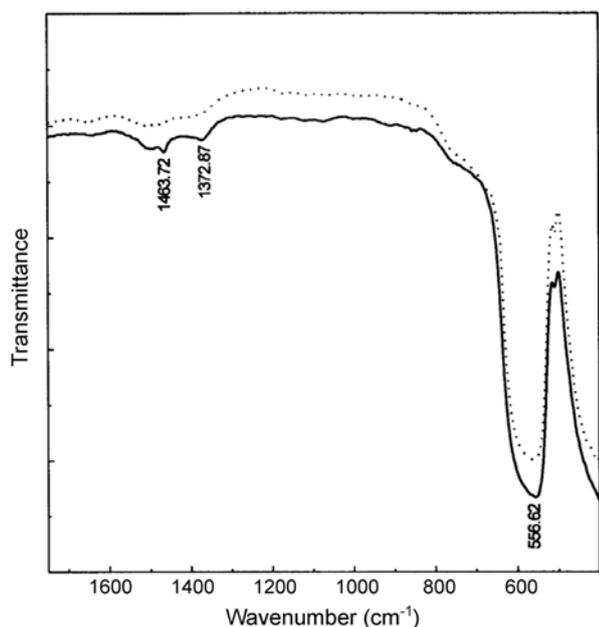


The X-ray diffraction pattern in Figure 1(C) shows monophase LaCoO<sub>3</sub> perovskite having rhombohedral structure. In Figure 2(C), the DSC curve of LaCoO<sub>3</sub> catalyst aged in air shows an endotherm peak at 310 °C, indicating the presence of lanthanum hydroxide. A small amount of lanthanum oxide might be isolated from the LaCoO<sub>3</sub>



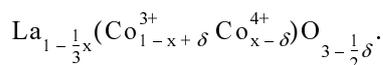
**Figure 5.** FT-IR spectra of La<sub>2</sub>O<sub>3</sub> catalyst after exposure to a CH<sub>4</sub>/O<sub>2</sub>/He mixture at 25 °C (dotted line) and 650 °C (solid line).

perovskite lattice by calcination at 850 °C in air. Though many authors have considered the LaCoO<sub>3</sub> system to be stoichiometric, several investigators pointed out the perovskite to be essentially nonstoichiometric.<sup>16,17</sup> O'Connel *et*



**Figure 6.** FT-IR spectra of LaFeO<sub>3</sub> catalyst after exposure to a CH<sub>4</sub>/O<sub>2</sub>/He mixture at 25 °C (dotted line) and 650 °C (solid line).

*al.*<sup>16</sup> found the isolated lanthanum oxide in the LaCoO<sub>3</sub> perovskite when the perovskite is prepared by precipitation from mixed nitrate solutions (La : Co atomic ratio of 1 : 1) using tetraethyl ammonium hydroxide and followed by calcination at 800 °C in He. As in the case of LaFeO<sub>3</sub> perovskite, when the Co<sup>3+</sup> ions partly convert to the Co<sup>4+</sup>, lanthanum-deficient LaCoO<sub>3</sub> perovskite can be formed. The Co<sup>4+</sup> cations is likely to be converted to the Co<sup>3+</sup> since the Co<sup>4+</sup> is unstable, resulting in the formation of oxygen vacancies in the perovskite. Then the perovskite can be written as



On the other hand, the LaNiO<sub>3</sub> catalyst showed different aspects from the LaFeO<sub>3</sub> and LaCoO<sub>3</sub> catalysts. In Figure 1(D), the XRD result of LaNiO<sub>3</sub> catalyst aged in air shows the presence of nickel oxyhydroxide (NiOOH). It can be assumed that when the LaNiO<sub>3</sub> perovskite is calcined in air at 850 °C, some nickel oxide is removed from the lattice and then, the isolated nickel oxide reacts with water vapor in air to form the nickel oxyhydroxide. In Figure 2(D), the DSC curve of LaNiO<sub>3</sub> catalyst aged in air shows a very weak endotherm peak at 230 °C and the endotherm is ascribed to dehydroxylation of nickel hydroxide. It is believed from the result that the nickel oxyhydroxide (Ni<sup>3+</sup>-OOH) contains a small amount of nickel hydroxide (Ni<sup>2+</sup>-(OH)<sub>2</sub>). When some nickel oxide is isolated from the LaNiO<sub>3</sub> lattice, the perovskite would be an oxygen-deficient oxide representing as La<sub>1</sub>Ni<sub>1-x</sub>O<sub>3-x</sub>.

In this context, it is worth noting that when LaBO<sub>3</sub> perovskites are calcined in air at 850 °C, lanthanum-

deficiencies are created in the LaFeO<sub>3</sub> or LaCoO<sub>3</sub> perovskite lattice while transition metal-deficiencies are created in the LaNiO<sub>3</sub> perovskite lattice, and the type of metal defects created in the perovskite is considered to depend on the oxidizability of transition metal ion (B<sup>3+</sup>) in air at high temperatures.

As described above, the present perovskite catalysts contain oxygen vacancies. The nature of active sites in metal oxide catalyst for the oxidative coupling of methane is not yet fully understood. However, it is generally accepted that less electrophilic oxygen species adsorbed on oxygen vacancy sites or highly basic surface lattice oxygen activate methane to generate methyl radicals and the resulting methyl radicals are coupled to form ethane in gas phase.<sup>18</sup> According to Domen *et al.*,<sup>19</sup> when gaseous oxygen is adsorbed on oxygen vacancies, super oxide species (O<sub>2</sub><sup>-</sup>) are formed immediately, successively converted into O<sub>2</sub><sup>2-</sup>, O<sup>-</sup>, and finally into O<sup>2-</sup> (latt).<sup>19</sup> Many investigators have suggested that in the oxidative methane coupling reaction over perovskite oxide catalysts, the existence of strongly bonded oxygen on the surface is effective to obtain more selectively C<sub>2</sub>-hydrocarbons from methane, in contrast to the weakly bonded oxygen necessary for deep oxidation of hydrocarbons.<sup>20-22</sup> Namely, weakly adsorbed molecular oxygen such as O<sub>2</sub><sup>-</sup> and O<sub>2</sub><sup>2-</sup> favors the formations of carbon oxides and less electrophilic oxygen species such as O<sup>-</sup> and O<sup>2-</sup> enhance the formation of methyl radicals leading to C<sub>2</sub> hydrocarbons. All these oxygen species adsorbed on the surface might exist in an equilibrium state and the concentration of less electrophilic oxygen species on the surface might depend on the temperature and oxygen partial pressure.

In this work, the differences in C<sub>2</sub>-selectivity of LaFeO<sub>3</sub>, LaCoO<sub>3</sub>, and LaNiO<sub>3</sub> catalysts seems to be closely related to their defect structures rather than their textual properties because their specific surface areas do not differ significantly as listed in Table 1. LaNiO<sub>3</sub> is known to be easily reduced by high temperature sintering<sup>23</sup> and the XRD result in Figure 1(D) reveals that the isolated nickel oxyhydroxide exists as a XRD detectable amount on the LaNiO<sub>3</sub> surface. Therefore, the LaNiO<sub>3</sub> perovskite can be assumed to contain more oxygen vacancies compared with the LaFeO<sub>3</sub> and LaCoO<sub>3</sub> perovskites. Since a high surface concentration of oxygen anion vacancies favours oxygen adsorption and transformation into less electrophilic oxygen species,<sup>22</sup> the LaNiO<sub>3</sub> catalyst is expected to show higher C<sub>2</sub>-selectivity than the other catalysts, but its C<sub>2</sub>-selectivity is lower than the other perovskite catalysts as shown in Figure 4. Its lower C<sub>2</sub>-selectivity seems to be due to the presence of isolated nickel oxide existing on the surface as an XRD detectable amount because nickel oxide is inactive for the oxidative coupling of methane.

Consequently, oxygen anion vacancies can be formed in the LaBO<sub>3</sub> perovskites by calcination at high temperatures in air without altermvalent cation doping. A mixture of isolated lanthanum oxide and lanthanum-deficient LaFeO<sub>3</sub> or LaCoO<sub>3</sub> perovskite shows higher C<sub>2</sub>-selectivity than a

mixture of isolated nickel oxide and LaNiO<sub>3</sub> perovskite for the oxidative coupling of methane. Although it is clear that oxygen anion vacancies play important role in the oxidative coupling of methane, the influence of isolated lanthanum oxide or isolated transition metal oxide on the nature of catalyst cannot be excluded. The formation of isolated lanthanum oxide or isolated transition metal oxide in the LaBO<sub>3</sub> catalysts under the reaction conditions and its role in the catalytic reaction require further research to be understood. It is necessary to study the ionic conductivity of perovskite in conjunction with its catalytic behavior above 700 °C because the mobility of oxygen ions in the perovskite is considered to relate to the formation of less electrophilic oxygen species on the surface and the study is currently in progress.

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