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The catalytic activity and surface characterization of $Ln_2B_2O_7$ (Ln = Sm, Eu, Gd and Tb; B = Ti or Zr) with pyrochlore structure as novel CH_4 combustion catalyst

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Abstract

$Ln_2B_2O_7$ (Ln = Sm, Eu, Gd and Tb; B = Zr or Ti) with pyrochlore structure was prepared by sol–gel method for the high-temperature catalytic combustion. The crystal structure of $Ln_2B_2O_7$ was identified by XRD and their surface area was about 4 m^2/g after calcinations at 1200 °C. Catalytic activity of methane combustion was observed for $Ln_2Zr_2O_7$ series and the best catalyst was $Sm_2Zr_2O_7$. Its relative reaction rate per unit surface area at 600 °C was 2 cm^3/m^2 min, which was twice higher than that of Mn-substituted Sr hexaaluminate. From surface analysis by XPS, the low binding energy of each Ln element of $Ln_2Zr_2O_7$ compared to that of $Ln_2Ti_2O_7$, gave the catalytic activity of methane combustion.

Keywords: Methane; XPS; $Ln_2Zr_2O_7$; Surface characterization; Pyrochlore structure; Catalytic combustion

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1. Introduction

It is well known that combustion catalyst can reduce the temperature of operation from 1500 to 1300 °C and suppress the NO_x formation [1]. There have been numerous studies on the application of high-temperature oxidation catalysts in gas-turbine power generation [2,3]. Among the most important properties are high combustion activity at typical combustor inlet conditions, thermal stability and high thermal shock resistance [4]. High activity can be obtained with catalysts that have a high catalyst surface area. Various promising materials, stable at high temperatures, have been reported in the literature [5]. A series of hexaaluminate were developed by Arai and coworkers [6]. Their sol–gel synthesized hexaaluminate ($BaAl_{12}O_{19}$ and $Sr_{0.8}La_{0.2}MnAl_{11}O_{19}$) exhibited a high thermal stability and catalyst activity at high temperature. Groppi et al. [7] achieved a similar performance when preparing the Mn-substituted barium hexaaluminate using a coprecipitation method. Pyrochlore ($A_2B_2O_7$) exhibits high chemical stability and catalytic activity at high temperatures in oxidative coupling of methane [8,9]. The application of pyrochlore as combustion catalysts was recently suggested since reasonable surface area and catalytic activity were observed in spite of the high-temperature treatment for the formation of pyrochlore structure [10].

In the present study, we prepared $Ln_2B_2O_7$ pyrochlore material for high-temperature combustion by

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the sol–gel method. Methane combustion and surface characterization were carried out in order to study the relation between catalytic activities and surface properties. The catalysts were characterized with XRD, N_2 BET method and XPS.

2. Experimental

2.1. Catalyst preparation

Pyrochlore materials ($Ln_2B_2O_7$; Ln = Sm, Eu, Gd and Tb; B = Zr or Ti) were prepared by the hydrolysis method of metal alkoxide. Calculated weight of zirconium isopropoxide (Aldrich, zirconium isopropoxide in isopropanol) or titanium isopropoxide (Aldrich Co., USA, 99.99%) was dissolved in 150 ml of isopropanol at 80 °C for 5 h under N_2 atmosphere. The stoichiometric amount of lanthanide metal (Ln = Sm, Eu, Gd and Tb) nitrate and water were dissolved in another 50 ml isopropanol. The amount of water was fixed according to the mole ratio of H_2O/M-OR of 2. The latter solution was slowly added to the former solution for about 15 min. This prepared gel was aged at 80 °C for 24 h, followed by the drying using the rotary evaporator at 80 °C. Dried gel was calcined in the flow of air at the rate of 2 °C/min to 1000, 1200, and 1400 °C and further calcined at each temperature for 2 h.

2.2. Characterization

(1) Surface area analysis and crystal structure analysis.

The surface areas of the sample were measured by BET method using N_2 adsorption. The crystal structures of the calcined sample were determined by X-ray diffraction (Regaku D/MAX-III) with Cu Kα radiation.

(2) Surface analysis.

XPS was performed with a SPECS LHS10 (Germany) Spectrometer. 0.1 g of samples was palletized and mounted on the sample holder. The XPS spectra were recorded using Al Kα radiation and the normal operating pressure inside the analyzer chamber was below 6.5×10^{-7} Pa. The binding energy was referenced to the binding energy of C 1s of 284.5 eV.

2.3. Catalytic combustion of methane

Catalytic activities were measured in a tubular flow type reactor at 1 atm. Gaseous mixtures of methane (1 vol.%) and air (99 vol.%) were premixed and fed to the reactor at the space velocity of 20,000 h^{-1}. Total gas flow rate was 50 cm^3/min. The methane conversion in the effluent gas was analyzed by on-line gas chromatography (DS6200, porapak Q column, TCD detector).

3. Results and discussion

3.1. Crystal structure analysis and surface area

Fig. 1 shows the XRD profiles of $Ln_2Ti_2O_7$ and $Ln_2Zr_2O_7$ calcined at 1200 °C for 2 h. Also, all samples have the pyrochlore structure similar to the reference materials without the formation of any impurities in the pyrochlore oxide. The change of the XRD intensity and the position of 2θ values were also examined according to the calcination temperature for $Sm_2Zr_2O_7$ (not shown). With the increase of the calcination temperature, the position of 2θ indicating pyrochlore structure was not changed and the intensity of each peak was growing. This means that during the calcination step, no other impure oxides like ZrO_2, Sm_2O_3 and so on were formed. Therefore, the samples before the calcination step, the two components (Sm and Zr) in the dried gel existed almost homogeneously. Typically, sol–gel techniques have an advantage over the conventional solid state reaction in that they enhance the homogeneity in the mixed precursor. The surface area of samples calcined at 1200 °C is shown in Fig. 2 including the values of all samples between 2 and 5 m^2/g. The surface area of $Ln_2Ti_2O_7$ obtained by solid state reaction was below 1 m^2/g [11]. The increase of surface area by the sol–gel method was also confirmed in the preparation of pyrochlore materials. However, the values of the surface area is much smaller than that of $Sr_{0.8}La_{0.2}Al_{11}O_{19}$ which is about 20 m^2/g [12]. Considering the conventional metal oxide perovskites used as a combustion catalyst had lost their surface area below 1 m^2/g, it could be thought that the pyrochlore materials could be used in high-temperature catalytic combustion.

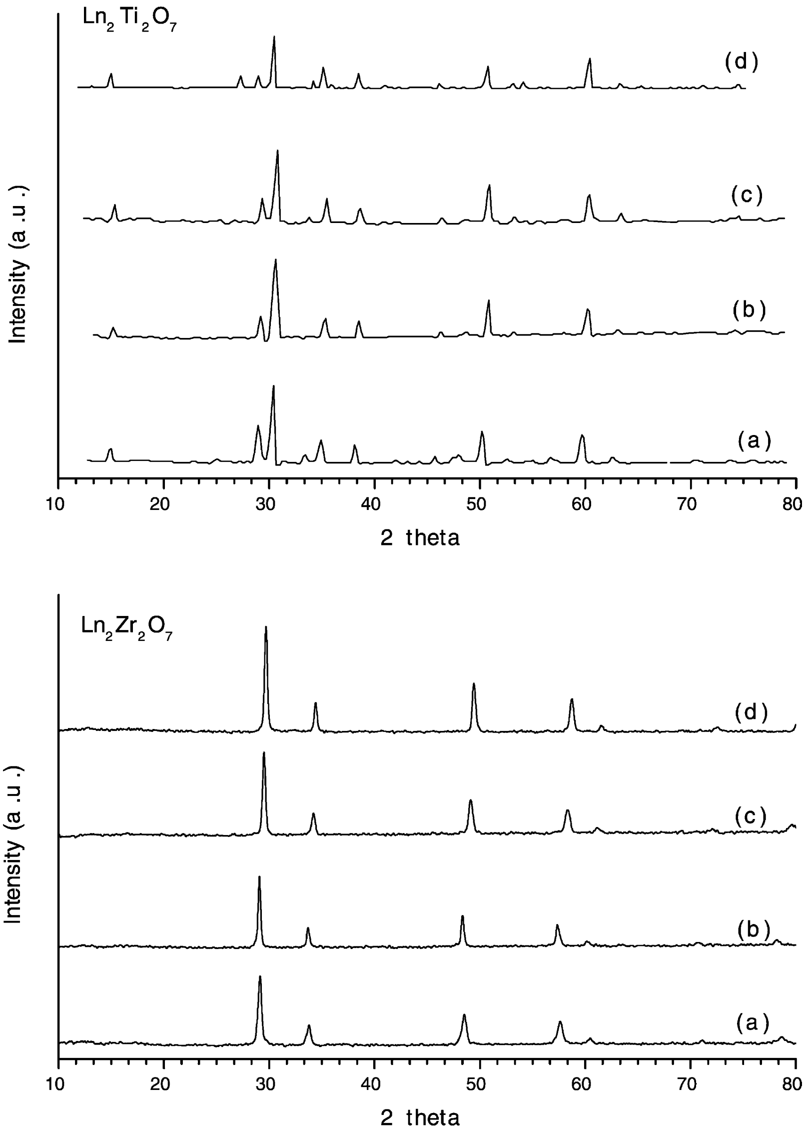

Fig. 1. XRD profiles of $Ln_2B_2O_7$ calcined at 1200 °C: (a) Ln = Sm, (b) Ln = Eu, (c) Ln = Gd, (d) Ln = Tb.

3.2. *Catalytic activity of $Ln_2B_2O_7$ ($A = Sm$, Eu, Gd, and Tb; $B = Zr$ or Ti)*

Fig. 3 shows the temperature dependency on CH_4 conversion over various pyrochlore samples prepared. In the case of $Ln_2Ti_2O_7$, their conversion profile was similar to the bulk reaction indicating that these materials did not show the catalytic activity on the CH_4 combustion. On the other hand, catalytic activity was shown for the $A_2Zr_2O_7$. Among a series of samples the best catalytic activity was shown for $Sm_2Zr_2O_7$. The $T_{10\%}$, which meant the temperature to reach the 10% conversion, was about 510 °C for $Sm_2Zr_2O_7$. The completion temperature ($T_{90\%}$) was about 700 °C for $Sm_2Zr_2O_7$. The activity order of samples at 50% conversion was $Sm_2Zr_2O_7 > Tb_2Zr_2O_7 > Gd_2Zr_2O_7 > Eu_2Zr_2O_7$. Comparing the results with consideration of the surface area of samples, the activity of CH_4

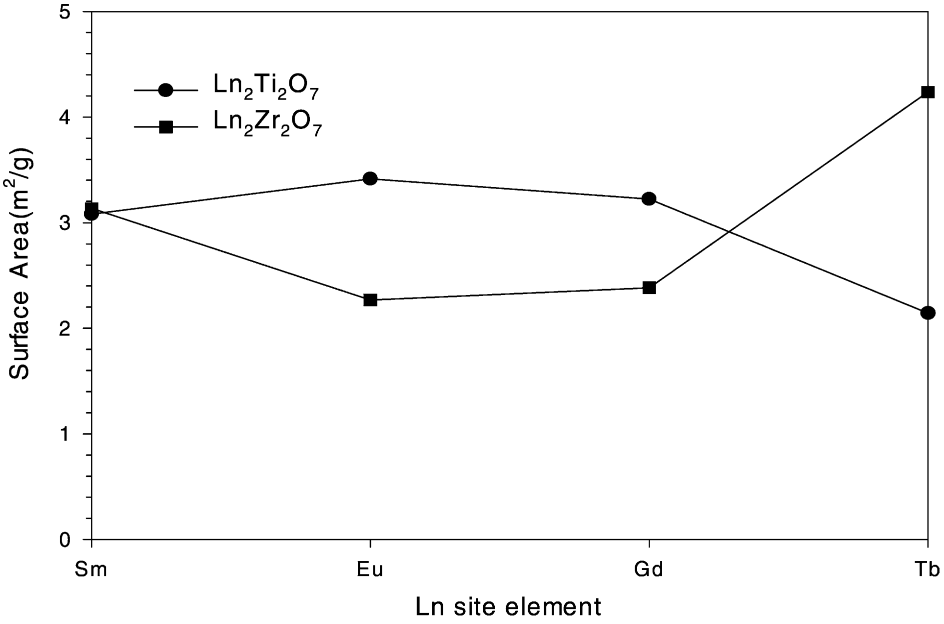

Fig. 2. Surface area of $Ln_2B_2O_7$ calcined at 1200 °C.

combustion might be dependent on the surface area of each sample. High surface areas could provide high catalytic activity. The Zr atom in B site seems to provide more active sites than the Ti atom, suggesting that catalytic activity is more influenced by the choice of B site atoms. Similar results were reported in the oxidative coupling of methane [9].

The relative reaction rate of $A_2Zr_2O_7$ (A = Sm, Eu, and Gd) calcined at 1200 °C was summarized in Table 1. The reaction rate per unit mass corresponds to the results of the conversion profile shown in Fig. 3. With the increase in the temperature, relative reaction rates were strongly increased indicating that gas phase reaction proceeded homogeneously with surface reactions on surface of the catalyst. The rate of the relative reaction rate per unit surface area was not increased compared to that of the relative reaction rate per unit mass. Though the lowest conversion of CH_4 at 600 and 700 °C was observed for $Eu_2Zr_2O_7$, the highest reaction rate per unit surface area was obtained because of its small surface area. That means that the overall reaction activity is strongly dependent on the surface area not on the reaction rate per surface area. Consequently, the most important factor to improve the catalytic activity must be the high surface area of a catalyst.

3.3. Surface analysis by XPS

In order to clarify the difference of the catalytic activity between $Ln_2Ti_2O_7$ (Ln = Sm, Eu, Gd, Tb) and $Ln_2Zr_2O_7$, the examination of the chemical state

Table 1
Comparison of relative activity at different temperatures

	$Sm_2Zr_2O_7$			$Eu_2Zr_2O_7$			$Gd_2Zr_2O_7$		
Temperature (°C)	600	650	700	600	650	700	600	650	700
Apparent activity per unit mass ($cm^3/g\,min$)	6.39	13.6	18.3	5.95	8.14	16.1	5.63	12.5	15.6
Apparent activity per unit surface area ($cm^3/m^2\,min$)	2.03	4.33	5.83	2.62	3.59	7.09	2.36	5.25	6.55

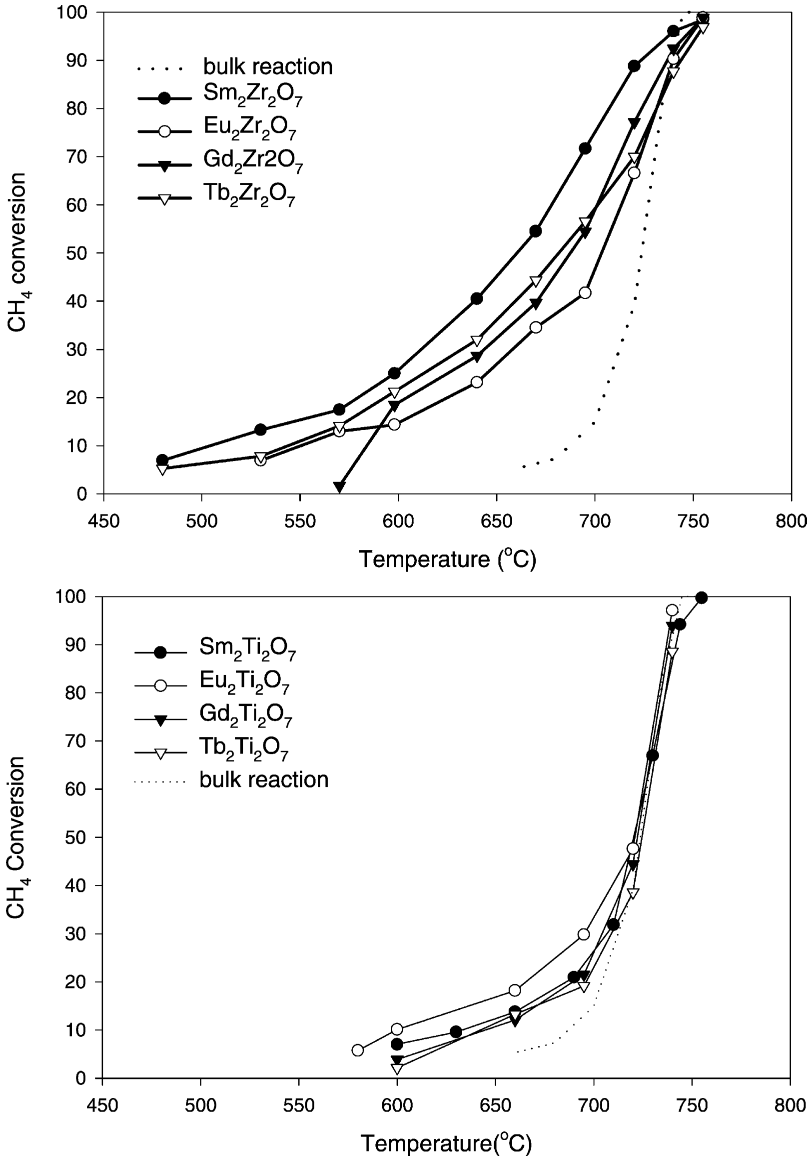

Fig. 3. CH_4 conversion profiles of $Ln_2B_2O_7$ calcined at 1200 °C.

Table 2
The binding energy (eV) of Ln element in the $Ln_2Zr_2O_7$ and $Ln_2Ti_2O_7$

	$Ln_2Zr_2O_7$				$Ln_2Ti_2O_7$			
Ln element	Sm $3d_{5/2}$	Eu $3d_{5/2}$	Gd $3d_{5/2}$	Tb $3d_{5/2}$	Sm $3d_{5/2}$	Eu $3d_{5/2}$	Gd $3d_{5/2}$	Tb $3d_{5/2}$
Binding energy (eV)	1082.5	1134.2	1186.7	1241.3	1082.8	1134.5	1187.2	1241.4
Reported binding energy (eV) of Ln^{3+} [19]	1083.5	1134.3	1187.5	1241.3				

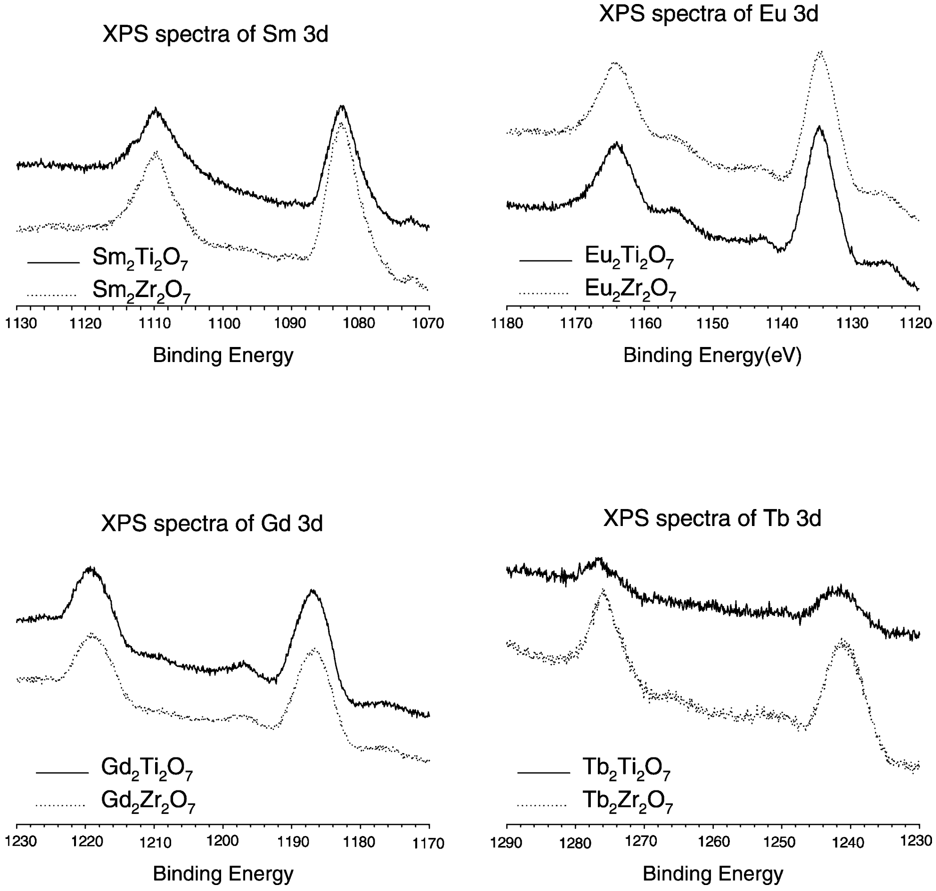

Fig. 4. XPS profiles of Ln 3d of $Ln_2B_2O_7$ calcined at 1200 °C.

on the surface of each element was performed by XPS. Fig. 4 shows the Ln_{3d} profiles of $Ln_2Ti_2O_7$ and $Ln_2Zr_2O_7$ in pyrochlore structure. The binding energy of each Ln element was summarized in Table 2. Theoretically, the oxidation state of the Ln element in the bulk state was +3. The binding energy of Ln species on the surface was lower than to that of the Ln^{3+} state except for Tb [13]. In the case of Sm and Gd, the surface oxidation state showed the presence of +2 and +3. This indicates that the oxidation state of the Ln element on the surface was lower than +3, which was the oxidation state in the bulk structure. For $Tb_2Ti_2O_7$, the oxidation state of Tb was +3. This result does not agree with the results reported by Christopher and Swamy [11] and vander Lean et al. [14]. As shown in Table 2, the smaller binding energy values of Ln element in $Ln_2Zr_2O_7$ compared with $Ln_2Ti_2O_7$ indicates the state of Ln element on the surface of $Ln_2Zr_2O_7$ has a lower oxidation state than that of $Ln_2Ti_2O_7$. In the case of Sm and Tb, the peak intensity of $Ln_2Zr_2O_7$ was higher than that of $Ln_2Ti_2O_7$ indicating that the more Ln species on the surface existed for $Ln_2Zr_2O_7$.

Fig. 5 shows the XPS profiles of Ti $2p_{3/2}$ and Zr $3d_{5/2}$. The binding energy of Ti $2p_{3/2}$ varied between 458.3 and 458.9 eV. It is reported [15,16] that titanium in the +4 oxidation state is found to have a binding energy value between 458 and 460 eV for the Ti $2p_{3/2}$ level. At that time, the oxidation state of Ti element in the $Ln_2Ti_2O_7$ was +4. Though small difference was observed in the binding energy of Ti 2p, it could be concluded that the typical oxidation state of Ti 2p on the surface of $Ln_2Ti_2O_7$ was almost same as the bulk state. In the case of $Sm_2Ti_2O_7$, Sm was less oxidized than +3 oxidation state suggesting

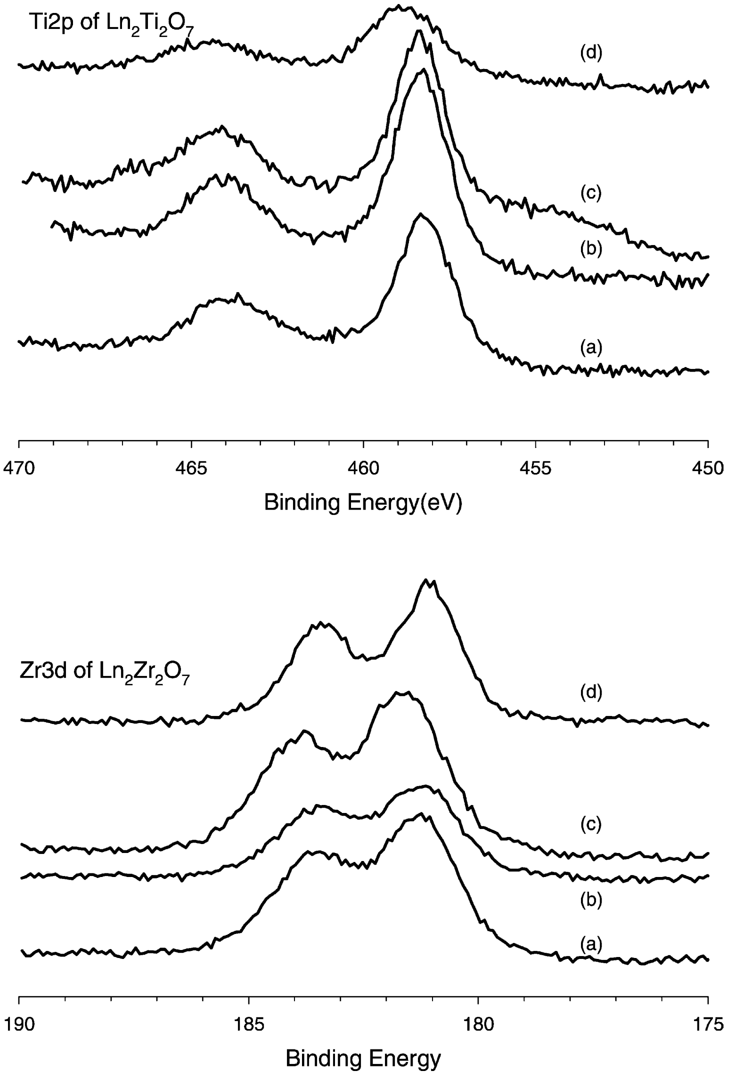

Fig. 5. XPS profiles of Ti 2p and Zr 3d of $Ln_2B_2O_7$ calcined at 1200 °C: (a) Ln = Sm, (b) Ln = Eu, (c) Ln = Gd, (d) Ln = Tb.

that the structure of $Sm_2Ti_2O_7$ on the surface might be different from the bulk state. The binding energy of Zr 3d also varied with the kind of Ln element. The observed binding energy of metal Zr $3d_{5/2}$ for Sm_2Zr_2O7 is 178.9 eV and the Zr^{4+} in the ZrO_2 crystal structure is 182.1 eV [13]. The binding energy of metal Zr $3d_{5/2}$ for Eu_2Zr_2O7, $Tb_2Zr_2O_7$ and $Gd_2Zr_2O_7$ was 181.1, 181.15 and 181.51 eV, respectively, which indicates that the oxidation state of Zr on the surface of $Ln_2Zr_2O_7$ lied between 0 and +4. Also, the Ln species on the surface of $Ln_2Zr_2O_7$ was not fully oxidized into the +3 state. Since the two elements, Ln and Zr, on the surface were not fully oxidized into +3 and +4, which was necessary for the formation of pyrochlore, the surface structure might be different compared to the bulk structure. Fig. 6 shows the O 1s profiles of $Ln_2Ti_2O_7$ and $Ln_2Zr_2O_7$ calcined at 1200 °C. For the $Ln_2Ti_2O_7$, two different oxygen species exist on the surface; one is represented at 532 eV, the other at 530 eV. However, new oxygen species were observed at 527 eV for the Ln_2Zr_2O7. Also, the relative concentration of oxygen species

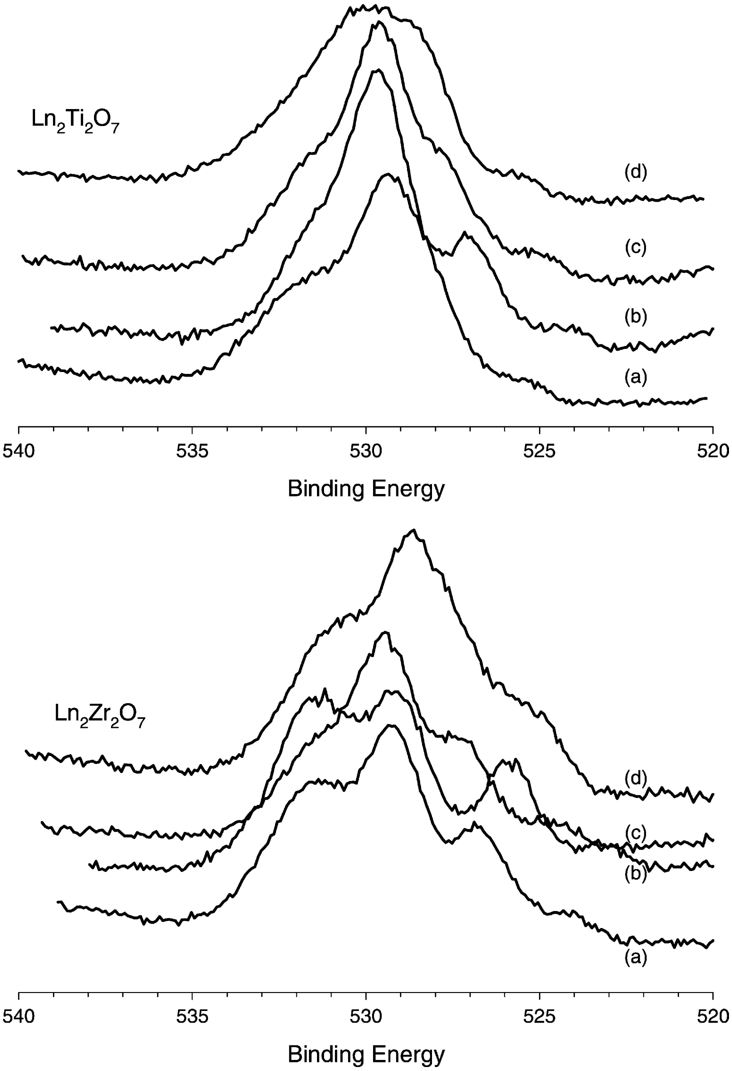

Fig. 6. XPS profiles of O 1s of $Ln_2B_2O_7$ calcined at 1200 °C: (a) Ln = Sm, (b) Ln = Eu, (c) Ln = Gd, (d) Ln = Tb.

of $Ln_2Zr_2O_7$ by comparison with peak intensities was increased by the substitution of Ti to Zr. The oxygen species at 530 and 532 eV represents the existence of O^{2-} and O^- or OH^-, respectively [11], but, it has not been reported what the peak at 527 eV represents. Since the O^{2-} species was observed at 530 eV, the oxygen state at 527 eV must be in an electron-rich state arising from the lattice structure. For the $Ln_2Zr_2O_7$, Ln and Zr on a surface were not fully oxidized into +3 and +4 and an electron-rich oxygen phase also existed. In order to match the electrical neutral state, it is suggested that the lack of oxygen species on the surface is expected, which does not satisfy the stoichiometry ratio of $Ln_2Zr_2O_7$. $Ln_2Zr_2O_7$ showed the catalytic activity for CH_4 reaction. Therefore, it is expected that the defect on the surface due to lack of oxygen species could provide the suitable catalytic activity for $Ln_2Zr_2O_7$. Otsuka et al. [17] have discussed the possible role of different oxygen species in the dimerisation of methane and it is suggested that the $O_2{}^{2-}$ and $O_2{}^-$ species may be involved in methane activation. Ashcroft et al. [8] suggested that the more selective catalyst have the common feature that in each case the rare-earth elements are able to exhibit mixed valence behavior: for Sm, Eu, and Gd, both the +2 and +3 oxidation states are known from the XPS study. From this result, the following reaction was proposed:

$$2Ln^{3+} + 2O_2{}^{-} = 2Ln^{2+} + O_2{}^{2-},$$
$$O_2 + O_2{}^{2-} = 2O^{2-}$$

Also, Petit et al. [18] proposed that the binding energy of (B–O) in pyrochlore structure strongly affected the C–H activation in the oxidative coupling of methane. Low binding energy could provide the higher C_2 selectivity and CH_4 conversion. Based on these suggestions, the relationship between the catalytic activity of CH_4 and the surface characterization of $Ln_2B_2O_7$ could be explained. It is concluded that the divalent state of the Ln element and the relatively high concentration of lattice oxygen species for $Ln_2Zr_2O_7$ shows the high catalytic activity in CH_4 combustion.

4. Conclusions

The pyrochlore structure was successfully formed by the sol–gel method. The temperature to form the crystal structure was lowered by 300 °C and its surface area was increased compared to typical solid state reactions. The crystal structure was observed after calcination at 800 °C. $Ln_2Zr_2O_7$ showed the catalytic activity for methane combustion, but $Ln_2Ti_2O_7$ did not. The activity of methane combustion of $Ln_2Zr_2O_7$ seems to be due to low binding energy of Ln species and Zr element on the surface of pyrochlores, which enable to have relatively higher oxygen concentration.

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