Catalytic combustion of methane over rare earth stannate pyrochlore

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Well-defined $Ln_2Sn_2O_7$ powders (Ln = La, Sm and Gd) with a phase-pure pyrochlore structure were synthesized by hydrothermal reaction. The catalytic activities of $Ln_2Sn_2O_7$ powders for methane combustion were measured. Methane oxidation started at 500 °C and increased with oxidation temperature. Catalytic methane combustion is strongly influenced by the presence of oxygen vacancies that form by breaking Sn–O lattice bonds as the temperature increases. Addition of manganese to the rare earth pyrochlores improved methane oxidation activity. Manganese-doped samarium stannate pyrochlore ($Sm_2Sn_{1.8}Mn_{0.2}O_7$) shows highest the catalytic activity. Light-off and complete oxidation temperatures were measured at about 400 and 650 °C, respectively.

KEY WORDS: catalytic combustion; methane; pyrochlore.

1. Introduction

Catalytic methane combustion attracts significant research interest for energy production purposes. Methane is a principal component of natural gas and it also burns much cleaner than other fuels. In spite of such advantages, methane combustion without catalysts requires very high temperatures because of its chemical stability. To solve the problem, many researchers have proposed catalytic flameless combustion. It is possible for catalytic methane combustion to occur at a temperature below 1000 °C, thereby reducing thermal NO_x formed during high-temperature combustion at above 1500 °C. Catalytic methane combustion eliminates emissions of pollutants such as CO, hydrocarbons and particulate matter (PM). It also promotes the complete catalytic oxidation of hydrocarbons, which permits stable operation under lean-fuel conditions and in turn improves energy efficiency [1–3].

Methane catalytic combustion requires well-controlled catalysts for practical applications such as gas turbines. Desirable characteristics of the catalyst materials include good catalytic activity, low light-off temperature, high thermal stability and large surface area. Noble metals such as Pd and Pt are mainly used as catalysts since they can reduce significantly methane combustion temperature [4]. However, noble metals are too expensive and not stable at high temperatures. Recently, alternative high-activity catalytic materials based on non-noble metal oxides, such as perovskite, hexaaluminate and pyrochlore oxide, have been investigated [5–10].

Pyrochlore-type oxides (general formula $A_2B_2O_7$) have attracted significant research interest for a wide variety of applications such as ionic/electronic conductors, catalysts, hosts for fluorescence centers, high-temperature pigments and radioactive waste [11]. In particular, some of the pyrochlores exhibit good catalytic activity and high thermal stability, which make them promising for catalytic combustion applications. In addition, it is possible to incorporate functional dopants to A or B sites in the pyrochlore lattice forming defect structures to improve catalytic activity [12]. In this work, we investigate the catalytic activities of rare earth stannate pyrochlores ($Ln_2Sn_2O_7$, Ln = La, Sm and Gd) for methane combustion.

2. Experimental

An equal molar amount of stannic chloride ($SnCl_4 \cdot xH_2O$) and rare earth nitrate ($Ln(NO_3)_3 \cdot 6H_2O$, Ln = La, Sm and Gd) was dissolved in deionized water. The metal salt solution was added dropwise into diluted aqueous ammonia solution by burette and stirred vigorously at room temperature. After stirring for 2 h the precipitates were centrifuged and washed four times with deionized water. As previously determined, good crystallization of phase-pure $Ln_2Sn_2O_7$ occurs only when the pH is above 10 [13,14]. Similarly, the pH of the feedstock for synthesizing rare earth stannate pyrochlore was adjusted to pH 10 by either NH_4OH or tetramethyl ammonium hydroxide. Hydrothermal reactions were performed at 200 °C for 36 h using a 500 ml-capacity autoclave with a magnetically driven stirrer (Model TPR-1, Taiatsu Techno). The as-synthesized product was washed and subsequently dried in an oven at 120 °C. Mn-substituted pyrochlores were obtained by adding manganese chloride tetrahydrate ($MnCl_2 \cdot 4H_2O$) and

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hydrogen peroxide (H_2O_2) during the feedstock preparation process. The crystal phase identification was determined by X-ray diffraction (XRD; Phillips APD1700) over a 2θ range of 10–70° at a scan rate of 2°/min. The chemical compositions of the products were measured using inductively coupled plasma spectrophotometry (ICP; Shimadzu, ICPS-100IV). The morphology of the product particles was examined using scanning electron microscopy (SEM; JEOL JSM6330F). The particle size and surface area of the powders were determined by a laser diffraction method (Nikkiso Microtrac HRA 9320-X100/UPA 9340) and the Brunauer–Emmett–Teller (BET) nitrogen adsorption technique (Coulter, Omnisorp 360), respectively.

The catalytic activity of rare earth stannate pyrochlores for methane combustion was measured using a fixed-bed microreactor (6 mm i.d.) under steady-state conditions at atmospheric pressure. An amount of 200 mg (125–355 μm size) of the catalyst sample powder was placed on a quartz wool plug and cleaned by pre-heat treatment at 800 °C in He for 1 h. The reactant gas mixture consisted of 1% O_2 and 0.2% CH_4 balanced by He. The total flow rate was 50 ml/min, at which the space velocity was about 10^5/h. The flow rate of each reactant gas was controlled by mass flow controllers (Bronkhorst, F-201C). Experiments were carried out at reaction temperatures from 200 to 700 °C, monitored by a K-type thermocouple in contact with the catalyst bed. The reactor was equilibrated for 30 min before any measurement at each temperature. CH_4, O_2 and CO_2 were analyzed by on-line gas chromatography (GC; Varian, MicroGC) to measure the amount of methane oxidation.

3. Results and discussion

The particle characteristics of the hydrothermally derived rare earth stannate pyrochlores are summarized in table 1. The mean particle sizes were in the range 0.25–0.59 μm, while the surface areas were approximately 14 m^2/g regardless of the type of rare earth elements. The results of XRD and ICP analysis indicate that the product powders were the well-crystallized single-phase pyrochlore with a relatively accurate stoichiometry. SEM observation revealed that the synthesized rare earth stannates have a relatively narrow size distribution and uniform shape with a rough surface structure, as shown in figure 1. Post-heat treatment after synthesis modified the particle characteristics. The surface areas varied as a function of heat treatment temperature. For example, the surface area of the as-synthesized $La_2Sn_2O_7$ decreased from 14.42 to 0.85 m^2/g as the heat treatment temperature increased to 1300 °C for 1 h in air. Furthermore, incorporation of Mn into the lattice decreased both the mean particle size and surface area for all the rare earth stannate pyrochlores.

Figure 2(a) shows the catalytic activities for methane oxidation over the rare earth stannate pyrochlores heat treated at 800 °C for 1 h. Methane oxidation started at about 500 °C and increased proportionally with oxidation temperature for all the catalysts. Methane oxidation over $Sm_2Sn_2O_7$ powders was completed at about 700 °C, whereas only 50% of methane was oxidized over $La_2Sn_2O_7$. The much better catalytic activities associated with both $Sm_2Sn_2O_7$ and $Gd_2Sn_2O_7$ catalysts result from their larger surface areas compared to $La_2Sn_2O_7$.

Figure 2(b) shows a normalized specific oxidation rate based on the surface areas of the rare earth stannates. In the case of the $La_2Sn_2O_7$ catalyst, the methane oxidation rate below 600 °C was lower than those of the $Sm_2Sn_2O_7$ and $Gd_2Sn_2O_7$ catalysts. However, the specific catalytic activity rapidly increased above 600 °C as compared to other stannates, so that the specific rate was 13.1×10^{-3} μmol/s/m^2 at 700 °C. This result indicates a relationship between the catalytic activity of methane oxidation and surface oxygen vacancies present on the catalyst. It is generally recognized that methane is preferentially absorbed on vacancy sites of the catalyst surface. The adsorbed methane undergoes dissociation into methyl or methylene radicals by hydrogen abstraction, and subsequently reacts with nearby absorbed oxygen to produce CO_2 and H_2O [1]. The higher methane oxidation activity of the rare earth stannates in the present study is likely to be associated with intrinsic oxygen vacancies (eight per unit cell) present in the pyrochlore lattice, which serve as active sites for methane adsorption and dissociation.

Table 1
Particle characteristics of the hydrothermally derived rare earth stannate pyrochlores

Sample	Mean particle size (μm)	Surface area as-synthesized (m^2/g)	Surface area after 800 °C, 1 h (m^2/g)	Surface area after 1100 °C, 1 h (m^2/g)	Surface area after 1300 °C, 1 h (m^2/g)
$La_2Sn_2O_7$	0.59 (±0.14)	14.42	4.13	1.37	0.85
$Sm_2Sn_2O_7$	0.19 (±0.05)	13.83	10.01	7.44	
$Gd_2Sn_2O_7$	0.25 (±0.06)	14.28	10.15	5.32	
$La_2Sn_{1.8}Mn_{0.2}O_7$	1.01 (±0.21)	2.92	2.93		
$Sm_2Sn_{1.8}Mn_{0.2}O_7$	0.25 (±0.05)	7.43	6.78		
$Gd_2Sn_{1.8}Mn_{0.2}O_7$	0.81 (±0.13)	6.59	5.76		

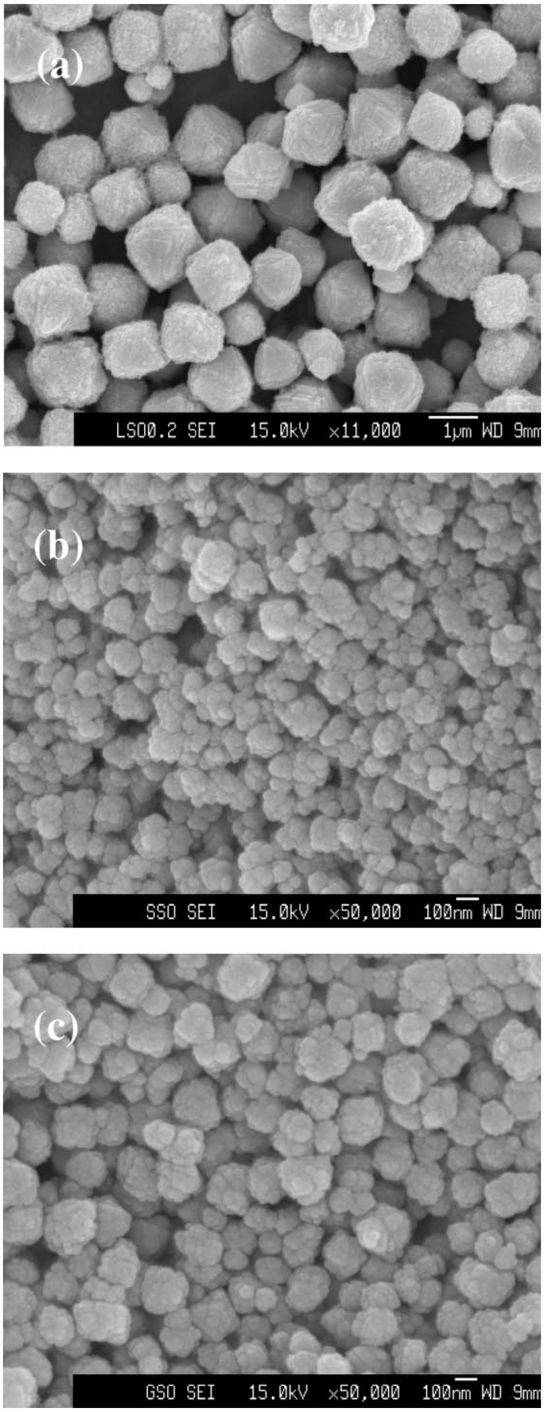

Figure 1. SEM micrographs of (a) $La_2Sn_2O_7$, (b) $Sm_2Sn_2O_7$ and (c) $Gd_2Sn_2O_7$ particles synthesized by a hydrothermal method at 200 °C.

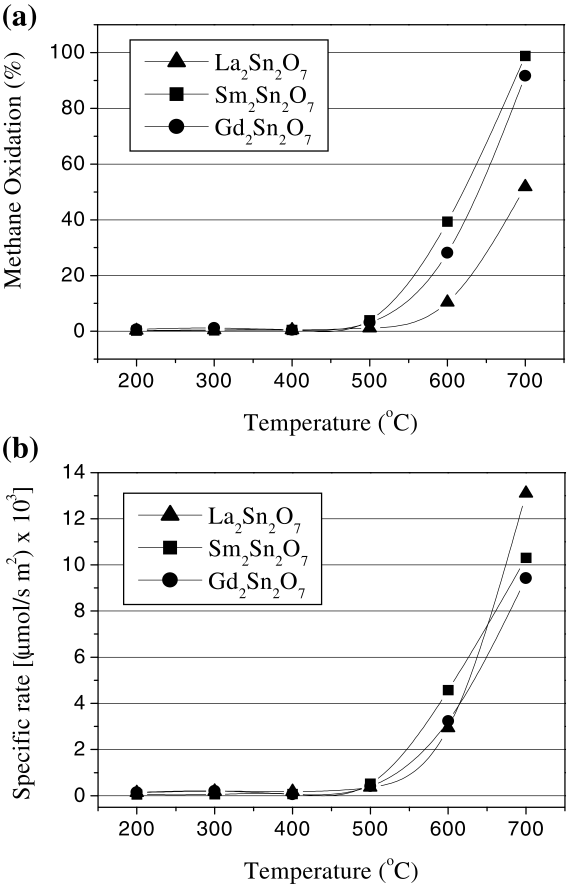

Figure 2. Methane oxidation behavior over rare earth stannate pyrochlores: (a) overall oxidation behavior based on the catalyst weight; (b) specific rate based on the surface area.

The different catalytic activities among the rare earth stannates above 600 °C are attributed to the relative ease in providing the surface oxygen vacancy formed by a breakage of the metal–oxygen lattice bond. It is believed that the rapid increase of the specific rate of methane oxidation above 700 °C for $La_2Sn_2O_7$ results from the presence of more oxygen vacancies per unit surface area, since Sn–O bond energy in the pyrochlore structure of $La_2Sn_2O_7$ is much lower than that in the other rare earth stannates. It has been reported, based on theoretical calculations of bond energy, that the difference in the Sn–O bond strength affects oxygen vacancy formation [15]. Bond energy calculations, based on Henry's equations as shown in table 2, reveal that lanthanide–oxygen (Ln–O) bonding energy is always higher than Sn–O, regardless of the type of rare earth elements. This indicates that the Sn–O bond is responsible for lattice oxygen release when sufficient thermal energy is provided for breaking oxygen lattice bonds. In this regard, the catalytic activity of methane oxidation increases with decreasing bond energy of Sn–O in the stannate pyrochlores, since the availability of surface oxygen vacancies is closely related to methane oxidation. Recently Teraoka *et al.* [12] have

Table 2
Structural information of rare earth stannate pyrochlores [15]

Ln	Lattice parameter (Å)	Bond energy ($\times10^{-8}$ coul^2/m)	
		Ln–O	Sn–O
La	10.702	13.376	6.349
Sm	10.508	13.528	6.370
Gd	10.450	12.484	6.433

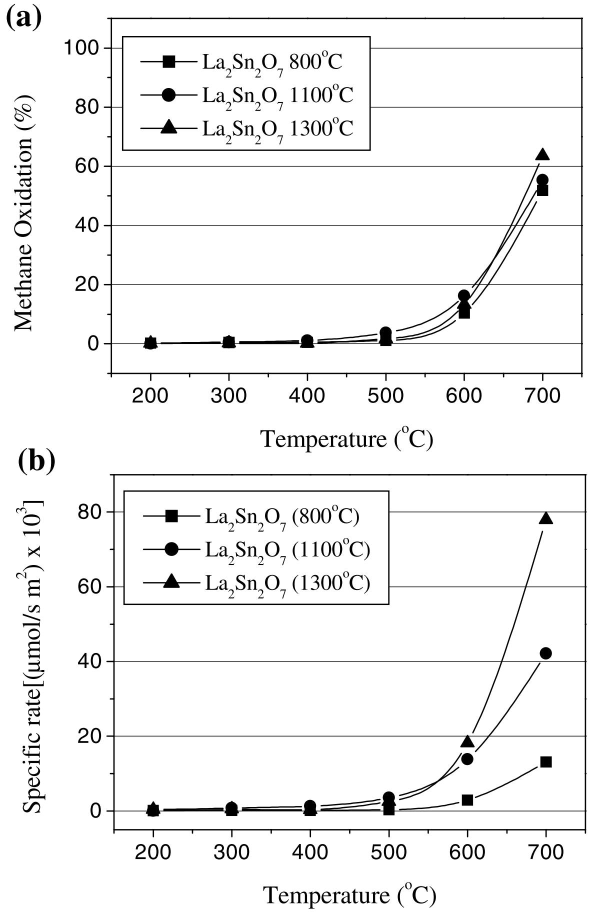

Figure 3. Methane oxidation behavior over $La_2Sn_2O_7$ catalysts heat treated at different temperatures: (a) overall oxidation behavior based on the catalyst weight; (b) specific rate based on the surface area.

reported, based on a temperature-programmed desorption (TPD) study, that the release of oxygen rapidly increases above 600 °C in the case of $La_2Sn_2O_7$, and the desorbed amounts are much higher than for other rare earth pyrochlores. Both theoretical and experimental findings support our observations regarding catalytic oxidation of methane, in which the specific rate of $La_2Sn_2O_7$ is higher at high temperatures.

Figure 3(a) shows the oxidation behaviors of methane over $La_2Sn_2O_7$ heat treated at different temperatures for 1 h. Methane oxidation normalized by catalyst weight exhibits similar catalytic activities, regardless of heat treatment temperature. It began at about 500 °C and increased proportionally with temperature. However, when based on the surface area of the catalyst, a much higher specific rate was observed for the catalyst heat treated at 1300 °C as compared to those heat treated at lower temperatures (figure 3(b)). This result implies that the generation of surface oxygen defects, by breaking lattice oxygen bonds in the vicinity of the surface, is promoted with increasing heat treatment temperature. More surface active sites are present in the catalyst heat treated at higher temperatures, which contributes to a higher specific rate of methane oxidation in spite of the reduced surface area.

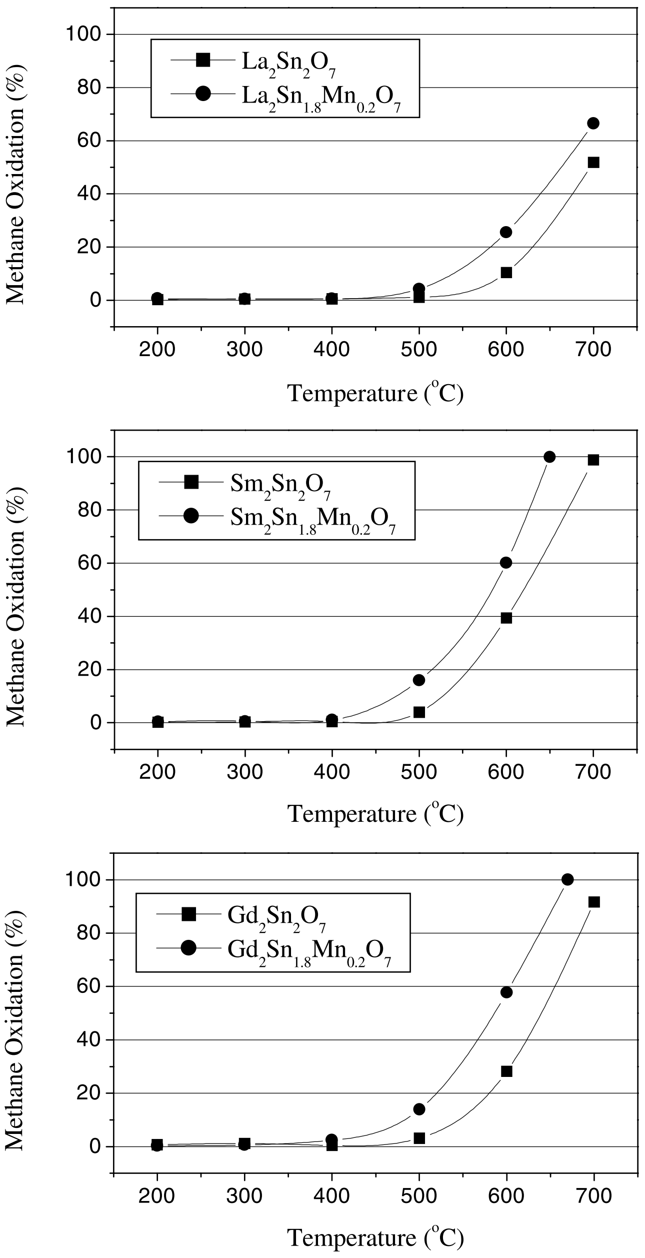

Figure 4. Comparisons of methane oxidation over the rare earth stannate pyrochlores with and without dopant.

Comparisons of methane oxidation over Mn-doped and undoped pyrochlores are shown in figures 4 and 5. The catalytic activities were improved remarkably by doping with Mn for all the rare earth stannates. Furthermore, light-off temperature at which methane oxidation begins decreased even though Mn doping reduced the surface area of the catalysts, as shown in table 1. It has been reported that transition metals, such as Mn, replacing Sn ions strongly modify the oxygen desorption and reduction behaviors [12]. The oxygen desorption of Mn-doped pyrochlore oxides started at a lower temperature than that of undoped pyrochlore oxides in a TPD study. The higher catalytic activity of Mn-doped pyrochlores is attributed to an increase in the surface

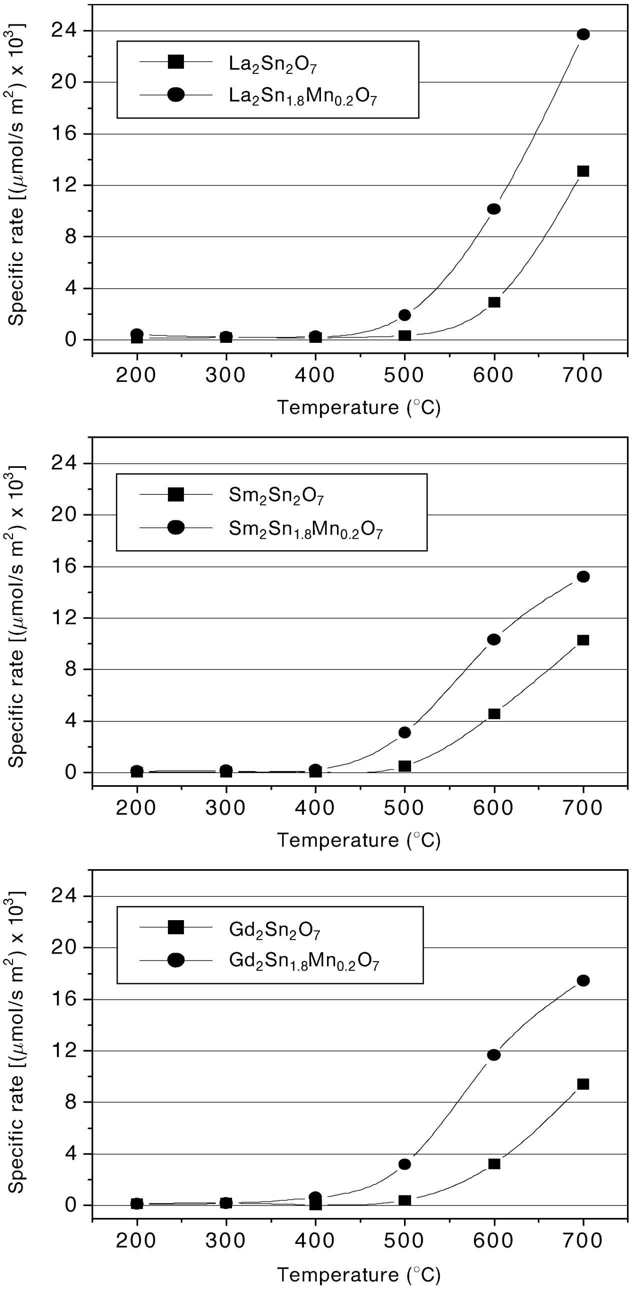

Figure 5. Comparisons of the specific rate based on the surface area of the rare earth stannate pyrochlores with and without dopant.

active sites upon addition of aliovalent dopant. The oxygen vacancy is generated in order to maintain charge neutrality when Sn^{4+} in the pyrochlore lattice is replaced by Mn^{2+} during doping.

4. Conclusion

Phase-pure rare earth stannate pyrochlores were synthesized by a hydrothermal method at temperatures as low as 200 °C. The resulting catalysts have a narrow distribution of particle size and a high surface area. The catalytic activity was closely related to the surface area of the catalyst and the oxygen vacancies on surfaces. The pyrochlore structure has intrinsic oxygen vacancies available as active sites for methane oxidation. Additional oxygen defects can be formed by breaking the lattice oxygen bonds during heat treatment at high temperatures, which is governed by the Sn–O bond strength in the rare earth stannate pyrochlores. The specific activity of methane oxidation for the $La_2Sn_2O_7$ catalyst was better than the others at about 700 °C, since the Sn–O bond energy of $La_2Sn_2O_7$ is much lower, which promotes more surface active sites present on the catalyst. When rare earth stannate pyrochlores were doped with the transition metal Mn, methane oxidation activity was significantly improved. Methane oxidation began at 400 °C and completed at about 650 °C for $Sm_2Sn_{1.8}Mn_{0.2}O_7$.

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