

Study on catalysts for combustion of lean CH₄

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Abstract— In this study, ceramics honeycomb-supported ABO₃ perovskite type oxides were prepared by changing the composition of A and B site cations, and observed their activities for lean CH₄ oxidation. In the case of change in A site composition La_{0.3}Sr_{0.2}MnO₃ and La_{0.6}Sr_{0.4}MnO₃ is the most active catalysts for 1 v% CH₄ and 2 v% CH₄, respectively. But LaMn_{0.5}Co_{0.5}O₃ oxide is the best active catalyst for 1–2v% CH₄ among the oxides by changing B site compositions of LaBO₃, and superior to La_{0.3}Sr_{0.2}MnO₃ and La_{0.6}Sr_{0.4}MnO₃ catalysts.

Adding trace Pd improved the activity and characteristics of space velocity for LaMn_{0.5}Co_{0.5}O₃ and La_{0.3}Sr_{0.2}MnO₃. Although LaMn_{0.5}Co_{0.5}O₃ + Pd (0.03 wt%) was less active than the Pd catalyst, the activity was more than Pt catalyst at a conversion level below 90%.

Keywords: catalysts; ABO₃ structure oxides; catalytic combustion; lean CH₄ oxidation.

1 Introduction

While exploiting coal a vast amount of CH₄ gas escaped, including a concentrated CH₄ gas (30–40v%) and a lean CH₄ gas (0.75–1v%). The amount of pure CH₄ discharged in the form of lean CH₄ gas during coal mining reached more than 5800 million Nm³ per year in China, corresponding to about 10 million tons of raw coal by heat value (Zhang, 1990). Great attention has been given to effective ways for using such energy resources. In addition, because CH₄ is a greenhouse effect gas, it must be treated before discharge. The lean CH₄ gas is a fuel of extremely low calorific value which only has 64–86 kcal/m³, and a stable combustion can not be carried out in common practice because the CH₄ concentration of the gas is below a lean flammability in air (5.3v%). Extremely lean combustion may be an effective technique for utilization of lean CH₄ gas energy resources and, moreover, catalytic combustion is a way of carrying out extremely lean combustion (Mizutani, 1985). Wang (Wang, 1989) puts forward a co-generation gas turbine plan using lean CH₄ gas as a working material, the unburned CH₄ is led to a catalytic combustion chamber for further burning in order to improve utilization efficiency of the lean CH₄ gas and save main fuel (Fig.1)

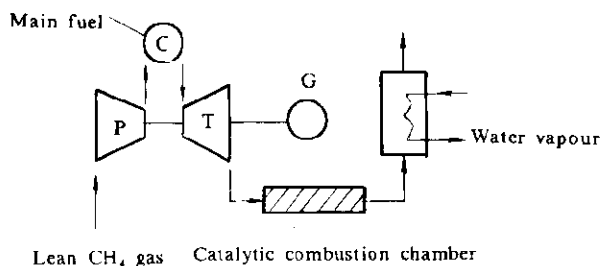


Fig. 1 Co-generation gas turbine plan for using lean CH_4

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Noble metals, such as Pt and Pd, are the lean CH_4 combustion catalysts in common use (JP; Wang, 1987), but recently great attention has been paid to transition metal oxides, especially ABO_3 structure oxides. Arai *et al.* (Arai, 1986) reported that rare earth LaBO_3 oxides ($B=\text{Co}, \text{Mn}, \text{Fe}$) showed high catalytic activity for CH_4 oxidation, and high activity was attained by partial A site cation substitution of LaMnO_3 ($\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$).

Catalytic activity of perovskite ABO_3 structure oxides is closely related to the properties of A and B sites cations. The cation sites in perovskite lattice can be easily substituted for foreign cations without a large change in structure. The substitution of foreign cations for A and/or B sites sometimes promotes the catalytic activity of perovskite type oxides.

In this study, honeycomb supported ABO_3 structure catalysts were prepared by impregnation, using La, Sr, Ag cations to adjust compositions of A site and Mn, Co, Cu cations to adjust compositions of B site. The catalytic properties of perovskite type oxides for lean CH_4 oxidation are investigated.

2 Experimental

Catalyst supports were prepared by using $\Phi 13 \times 30$ mm/mm honeycomb ceramics as matrix, and thermally stable and high surface area materials as washcoat. The amount of washcoat coated on supports was more than 10 wt% and peeling strength of washcoat was less than 0.5 wt%. Perovskite type oxides were prepared

by impregnating supports with water solutions of mixed metal nitrates, and subsequent drying, decomposition of nitrates at 300°C and calcination at 800°C for 2 hours. The supported amount of oxides was more than 10 wt%, and surface area of catalysts was 6–8 m²/g. XRD patterns of calcined samples showed that the perovskite phase was partially formed in the prepared oxide mixtures except for Ag-added oxides from which free Ag was separated. The ABO₃ + Pd (0.03 wt%) catalysts were further prepared by impregnation of ABO₃ oxides catalysts in PdCl₂ water solution and subsequent drying and calcination at 560°C for 3 hours. Honeycomb Pt (2.12 g/L) and Pd (2.06 g/L) catalysts were prepared by impregnation with calcination at 550°C for 4 hours. The catalysts was fixed in a quartz tube and placed in an electric furnace. The reaction temperature was monitored by a thermocouple. A gaseous mixture of CH₄ and air was fed into the reactor at a SV=10000 h⁻¹. The concentration of CH₄ at inlet and outlet of reactor were analyzed by gas chromatography and conversion of CH₄ oxidation was calculated.

3 Results and discussion

3.1 Effect of changing B site cations on activity of LaBO₃ oxides

A variety of LaBO₃ structure oxides are prepared by changing B site cations which are a single cation of Co, Mn, Cu or two cations of Co-Mn, Co-Cu, Mn-Cu, or all three of Co-Mn-Cu. The compositions of B site cations are quantitatively shown in a composition triangle (Fig.2). The activity of the catalyst was evaluated as the temperature at which 50% and 90% conversions of CH₄ oxidation were attained. The relationship between T_{90%} (°C) of 1 v% CH₄ oxidation and composition of B site cations (Fig.3) indicates that: (1) on the LaBO₃ oxides in which B site cations are made up of Mn-Co the oxidation activity of 1 v% CH₄ is better than the other B site composition systems, and among them, LaMn_{0.5}Co_{0.5}O₃ oxide (i.e. Mn/Co=1 atom ratio) has the best oxidation activity; (2) in the case of LaBO₃ oxides in which B site cations are three cations systems of Cu-Mn-Co and the content of Cu is equal to 0, 0.2, 0.6, 0.8 (atom%), yet the LaMn_{0.5}Co_{0.5}O₃ oxide (i.e. Cu=0) is the best catalyst for 1 v% CH₄ oxidation. From T_{50%} data the same results were obtained.

3.2 Effect of changing A site cations on activity of ABO₃ oxides

On the basis of B site composition, a variety of La_{1-x}A_xMn_{0.5}Co_{0.5}O₃ oxides in which A_x is Sr, Ag or Sr-Ag were prepared, and a number of La_{1-x}Sr_xBO₃ oxides in which B cation is Co or Mn were also prepared. The composition of A site cation is quantitatively shown in a composition triangle (Fig.2b).

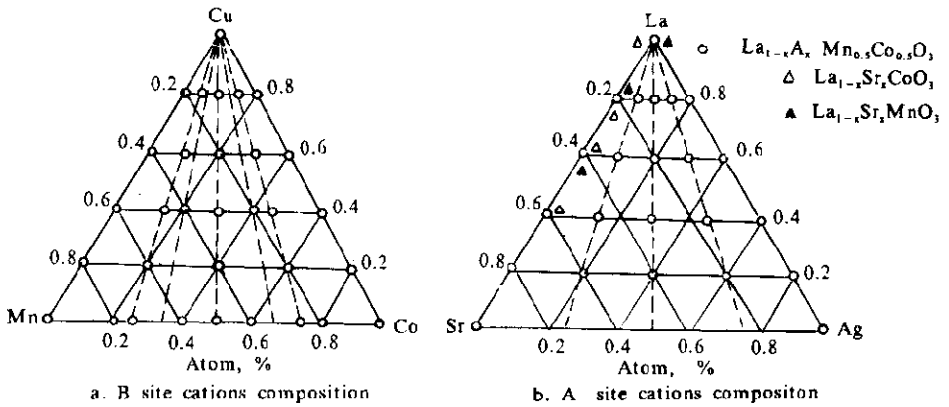


Fig. 2 composition triangle

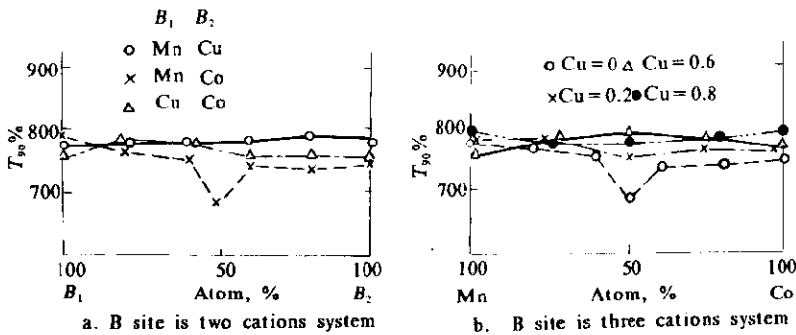


Fig. 3 Relationship between activity and composition of B site cations

The relationship between $T_{50\%}$ of 1 v% CH₄ and A_x site compositions is shown in Fig. 4. It shows following activity sequence: $La_{0.4}Ag_{0.6}Mn_{0.5}Co_{0.5}O_3 > LaMn_{0.5}Co_{0.5}O_3 > \dots > La_{0.8}Sr_{0.2}MnO_3 > La_{0.2}Sr_{0.8}Mn_{0.5}Co_{0.5}O_3 > \dots > La_{0.8}Sr_{0.2}CoO_3 > \dots > La_{0.6}Sr_{0.4}MnO_3 > \dots$. The results of 2 v% CH₄ oxidation on various catalysts ($T_{50\%}$) show following activity sequence: $La_{0.2}Sr_{0.2}Ag_{0.6}Mn_{0.5}Co_{0.5}O_3 > LaMn_{0.5}Co_{0.5}O_3 = LaMnO_3 > La_{0.6}Sr_{0.4}MnO_3 > La_{0.8}Sr_{0.2}MnO_3 > LaCoO_3$ (Table 1). As stated above, when Ag exist in A site, the ABO₃ structure oxides were not formed, so among the rare earth ABO₃ prepared by changing A site cations, $La_{0.8}Sr_{0.2}MnO_3$ is the best catalyst for 1 v% CH₄ oxidation, and $La_{0.6}Sr_{0.4}MnO_3$ is the best one for 2 v% CH₄ oxidation. The latter results agree well with those of Arai (Arai, 1986).

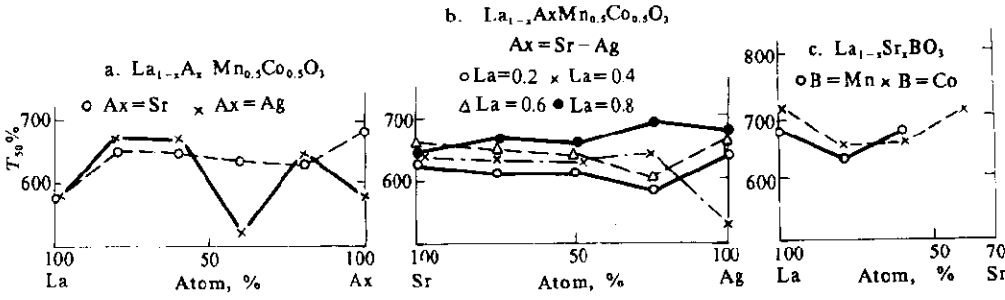


Fig. 4 Relationship between activity and composition of A site cations

Table 1 The results of 2 v% CH_4 oxidation

Catalysts						T _{50%}
A site		B site				
La	Sr	Ag	Mn	Co	Cu	
1	0	0	0	1	0	550
1	0	0	1	0	0	522
1	0	0	0.5	0.5	0	522
0.8	0.2	0	1	0	0	540
0.6	0.4	0	1	0	0	536
0.2	0.2	0.6	0.5	0.5	0	478

3.3 Effect of adding trace Pd on activity of ABO_3 oxides

$\text{LaMn}_{0.5}\text{Co}_{0.5}\text{O}_3 + \text{Pd}$ (0.03 wt%) and $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3 + \text{Pd}$ (0.03 wt%) catalysts were prepared from $\text{LaMn}_{0.5}\text{Co}_{0.5}\text{O}_3$ and $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ by impregnation method. The results of oxidation activities of 1 v% or 2 v% CH_4 on them at $\text{SV}=10000 \text{ h}^{-1}$ are shown in Table 2.

The activity and space velocity characteristics for CH_4 oxidation are improved evidently by addition of trace Pd. The characteristics of space velocity for CH_4 oxidation on the $\text{LaMn}_{0.5}\text{Co}_{0.5}\text{O}_3$ and $\text{LaMn}_{0.5}\text{Co}_{0.5}\text{O}_3 + \text{Pd}$ (0.03 wt%) catalysts are shown in (Fig.5).

Tbale 2 Activities of CH₄ oxidation on Pd-added catalysts

Catalysis	T _{50%}	T _{90%}	Concentration of CH ₄ , v%
La _{0.8} Sr _{0.2} MnO ₃	630	715	1
La _{0.8} Sr _{0.2} MnO ₃ + Pd	435	500	
LaMn _{0.5} Co _{0.5} O ₃	585	685	
LaMn _{0.5} Co _{0.5} O ₃ + Pd	465	615	
La _{0.8} Sr _{0.2} MnO ₃	540	570	2
La _{0.8} Sr _{0.2} MnO ₃ + Pd	480	556	
LaMn _{0.5} Co _{0.5} O ₃	522	553	
LaMn _{0.5} Co _{0.5} + Pd	422	456	

Note: Pd 0.03wt%

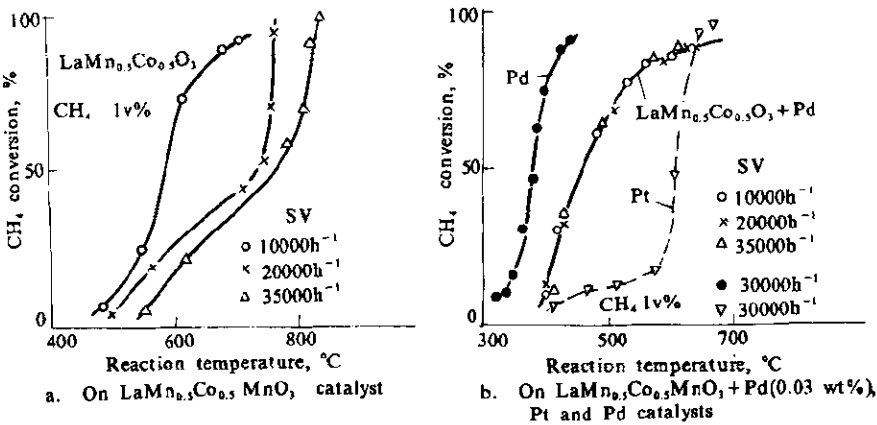


Fig. 5 Activity and space velocity characteristics for CH₄ oxidation

Fig. 5 indicates that the activities for 1 v% CH₄ oxidation on LaMn_{0.5}Co_{0.5}O₃ were lowered with increasing space velocity within 10000–35000 h⁻¹, but in the case of LaMn_{0.5}Co_{0.5}O₃ + Pd (0.03 wt%) the change in activities was not clear. Temperature

dependence for 1 v% CH₄ oxidation at SV=30000h⁻¹ over Pt and Pd catalysts are shown in Fig. 5b. Although LaMn_{0.5}Co_{0.5}O₃+Pd (0.03 wt%) was less active than the Pd catalyst, the catalytic activity was more than Pt catalyst at a conversion level below 90%.

4 Conclusions

A large number of ceramics honeycomb-supported ABO₃ perovskite type oxides were prepared by changing the composition of A and B site cations, and observed their activities for lean CH₄ oxidation. Some of rare earth ABO₃ oxides are highly active, especially when cations of A and B sites in them are substituted partially. In the case of change in A site composition La_{0.8}Sr_{0.2}MnO₃ and La_{0.6}Sr_{0.4}MnO₃ is the most active catalyst for 1 v% CH₄ and 2 v% CH₄, respectively. But LaMn_{0.5}Co_{0.5}O₃ oxide is the best active catalyst for 1–2 v% CH₄ among the oxides by changing B site compositions of LaBO₃, and superior to La_{0.8}Sr_{0.2}MnO₃ and La_{0.6}Sr_{0.4}MnO₃ catalysts.

Adding trace Pd improved the activity and characteristics of space velocity for LaMn_{0.5}Co_{0.5}O₃ and La_{0.8}Sr_{0.2}MnO₃. Although LaMn_{0.5}Co_{0.5}O₃+Pd (0.03wt%) was less active than the Pd catalyst, the activity was more than Pt catalyst at a conversion level below 90%.

Further research will be focused on the preparation method of Pd-added LaMn_{0.5}Co_{0.5}O₃ catalyst, optimum addition amount of Pd and their durability in reaction in order to obtain excellent practical catalysts for lean CH₄ combustion.

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