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Recent advances in high temperature catalytic combustion

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Abstract

Catalytic combustion of methane has been investigated for the application to gas turbines. As the combustion is operated at high temperatures and high space velocity, heterogeneous reaction and surface-initiated gas phase reaction proceed concurrently. Thermal resistance to maintain large surface area is, therefore, requested to attain high combustion efficiency above 1000°C. Hexaaluminate compounds were effective in maintaining large surface area. On the other hand, palladium catalysts were generally employed for the combustion of methane below 1000°C. The prototype catalyst combustors were successfully tested with their high combustion efficiency and low NO_x emission by using Pd based- and/or hexaaluminate catalysts.

Keywords: Pd catalysts; Hexaaluminate catalysts; Combustion of methane

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1. Introduction

Catalytic combustion of hydrocarbons has been investigated extensively so far for the reaction temperature below 1000°C. The catalytic combustion around or above 1000°C has not been investigated satisfactorily because of the lack of heat resistant catalysts, however, the catalyst materials being operated at such high temperatures has been attracting attention recently for application to natural gas fueled gas turbines [1,2]. The combustion temperature for gas turbine can be reduced by using an active catalyst without deteriorating combustion efficiency and also stable combustion becomes possible even for a fuel lean condition. The most attractive advantage of the catalytic combustion is the reduction of thermal NO_x emission as shown in Fig. 1. For the normal flame combustion, the temperature in the combustion zone reaches above 1500°C where thermal NO_x is produced by the reaction between N_2 and O_2. Therefore, the selective catalytic reduction (SCR) catalyst is placed at the outlet of the exhaust gas. The catalytic combustion, however, significantly reduces the operation temperature; thus, thermal NO_x is scarcely produced. The combustion becomes more stable as compared to the flame combustion even in the lean burn condition, therefore, high efficiency can be attained. From these characteristics, the catalytic combustion at high temperatures has been attracting great interests as well as that at low and medium temperatures. In this paper, recent developments in high temperature catalytic com-

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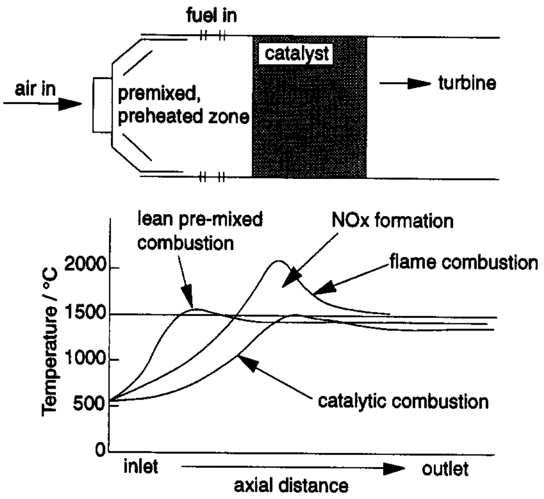


Fig. 1. Schematic profiles of temperature and NO_x emission in a combustor.

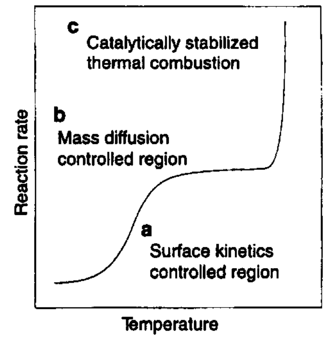


Fig. 2. Temperature dependence of overall reaction rate in catalytic combustion.

bustion are summarized, especially focusing on the research of catalyst materials.

2. Reaction characteristics of catalytic combustion

We have been developing hexaaluminate-related compounds for application to high temperature combustion [3–5]. For the combustion catalysts operated at a high space velocity, a large catalyst surface is a desired factor to attain high conversion at a short contact time. Especially at high temperatures, the number of active site and, hence, the large active surface area is important, since, the activity of each catalytic site is already enhanced. However, for the combustor with extremely high feed rate, complicated combustion process should be taken into account since the effect of mass diffusion appears seriously. It is generally known that the activity of catalytic combustion follows the temperature dependence shown in Fig. 2. In the low temperature region, the surface reaction over a catalyst enhances the conversion exponentially with a rise in temperature. In the medium temperature region, however, the increase in catalytic activity is suppressed, since, the mass diffusion of the reactant to the active surface becomes rate limiting. At high temperatures, the conversion rises up very sharply and the gas phase radical combustion proceeds concurrently with the surface reaction. The sharp rise in conversion is characteristic for the gas phase reaction.

The temperature dependence of catalytic combustion is strongly affected by the space velocity of the reaction, since, the reaction is operated with a very high flow rate. The combustion curve like Fig. 2 could be reproduced experimentally by diluting an active catalyst with inactive alumina beads (Fig. 3). $Sr_{0.8}La_{0.2}MnAl_{11}O_{19-\alpha}$ (SLMA) was used as

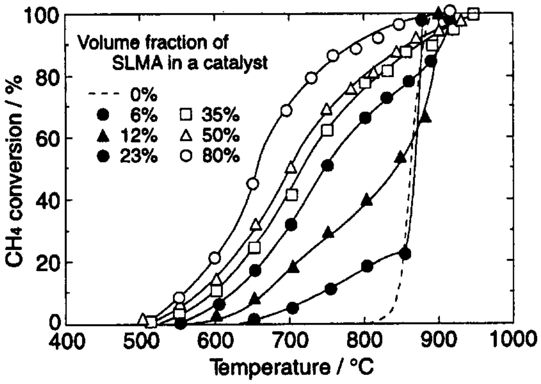


Fig. 3. Catalytic combustion of methane over SLMA and α-Al_2O_3 mixtures. Reaction condition; CH_4, 1 vol.-%; air, 99 vol.-%; SV = 48000 h^{-1}.

the catalyst with high thermal stability. The catalytic properties of this sample will be explained later. In this experiment, the volume of the catalyst bed and gas flow rate were fixed, but the volume fractions of SLMA and alumina were subject to change. In the case of high content of SLMA (80 vol.-%), the combustion initiated from low temperature (< 500°C); then, the activity monotonously increased with a rise in temperature. The increase in activity became gradual only in the high conversion region above 80%, corresponding to the mass diffusion controlled region. As the fraction of SLMA decreased, the conversion was generally lowered in low and medium temperature regions. In the case of 12 vol.-% SLMA, the slope of the activity curve becomes very gradual in the conversion range between 40% and 60%, in which the mass diffusion to the catalyst began to control the rate of the reaction. Then, the activity again increased very steeply at higher temperatures. This means that surface-initiated gas phase reaction started. It is noted that the temperature for the 100% conversion was high for reaction with a high catalyst content (35–80 vol.-%) than that with a high dilution rate (0–6 vol.-%).

These results indicate that the high activity and high surface area are requested for the catalyst to initiate and stabilize combustion. But the sole catalytic process is insufficient; i.e., the combination of the catalytic and gas phase combustion is effective in attaining high combustion efficiency and stable combustion, since the activity curve rose up quite steeply for the gas phase homogeneous reaction. Since the dilution of the active catalyst is regarded as operation at high space velocity, the surface catalytic reaction and concomitant surface-initiated gas phase reaction is operative in the practical case at space velocity of 500000 h^{-1} or higher. However, for the material research on catalytic activity and thermal stability such a severe reaction condition is difficult to achieve in the small scale reactor. The basic properties of catalyst materials are, therefore, obtained at SV = 48000 h^{-1} in the present study.

3. Catalyst materials for high temperature combustion

3.1. Activity and thermal stability of mixed oxide catalysts

As mentioned above, the mass diffusion process to the catalyst surface significantly influences the rate of combustion. A large active surface area per volume of catalyst is, therefore, naturally requested to treat a vast amount of fuel. Table 1 summarizes the surface area of several heat resistant oxides to look for the candidate for a catalyst support. It is noted that the system $BaO-Al_2O_3$ attained the largest surface area after heating at 1450°C.

Metal dispersed catalysts have been known to be active in the low and middle temperature regions. When a metal-supported oxide with a large surface area is used as a catalyst at high temperatures above 1000°C, the catalyst undergoes sintering and/or evaporation of the metallic component. From these reasons, a catalyst material for the high temperature application preferably consists of an equilibrium phase with a uniform composition. The active component is doped directly in the lattice of the structural material which retains large surface area even at high temperatures.

We have developed the hexaaluminate-based compounds as catalysts for high temperature

Table 1
Surface areas of mixed oxides after calcination at 1450°C

Support	Surface area /m^2 g^{-1}
Al_2O_3	1.4
$(BaO)_{0.1}(Al_2O_3)_{0.9}$	4.5
$(MgO)_{0.1}(Al_2O_3)_{0.9}$	1.2
$(ZrO_2)_{0.1}(Al_2O_3)_{0.9}$	1.0
ZrO_2	0.8
$(MgO)_{0.1}(ZrO_2)_{0.9}$	0.3
$(CaO)_{0.1}(ZrO_2)_{0.9}$	0.9
$(Al_2O_3)_{0.1}(ZrO_2)_{0.9}$	0.5
MgO	9.6
$(Al_2O_3)_{0.1}(MgO)_{0.9}$	1.0
$(SiO_2)_{0.1}(MgO)_{0.9}$	1.3
$(Cr_2O_3)_{0.1}(MgO)_{0.9}$	1.5

combustion based on the above consideration. The composition dependence of surface area of the system Ba–Al oxide is shown in Fig. 4. Powders of γ-Al_2O_3 and $BaCO_3$ were mixed with a predetermined ratio and subsequently heated at 1450°C. The X-ray diffraction pattern indicated that all the samples after heating at 1450°C consisted of the equilibrium phase, i.e., single phase of α-alumina, BaO–6Al_2O_3, and BaO–Al_2O_3 for $x = 0$, 0.14 and 0.5, respectively, and the mixture of them between these compositions. The surface area was maximum at $x = 0.14$, at which the single phase of barium hexaaluminate, BaO–6Al_2O_3, is the equilibrium. It is surprising that the melting point of Al_2O_3 is significantly higher then that of BaO–6Al_2O_3, but the surface area was smaller for Al_2O_3.

The surface area of alumina significantly decreased with increasing calcination temperature as shown in Fig. 5. The decrease is related with the phase change from γ- into α-alumina. The surface area of BaO–6Al_2O_3 was larger than Al_2O_3, but was much influenced with the preparation procedure of the powder. The surface area of BaO–6Al_2O_3 was large when this material was prepared from alkoxides hydrolysis. The difference in surface area between two preparation routes is due to the mixing of Ba and Al components in the precursor state. For the sample obtained by powder calcination, an intermediate Ba–Al_2O_4 phase appeared. During the course of the intermediate phase formation, the surface area was reduced significantly by grain growth before the hexaaluminate formation was completed. Therefore, mixing at the atomic level is requested in the precursor state by employing alkoxides-hydrolysis process.

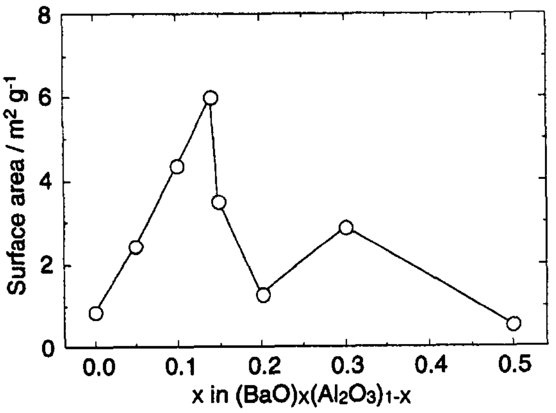


Fig. 4. Surface areas of $(BaO)_x(Al_2O_3)_{1-x}$ system calcined at 1450°C.

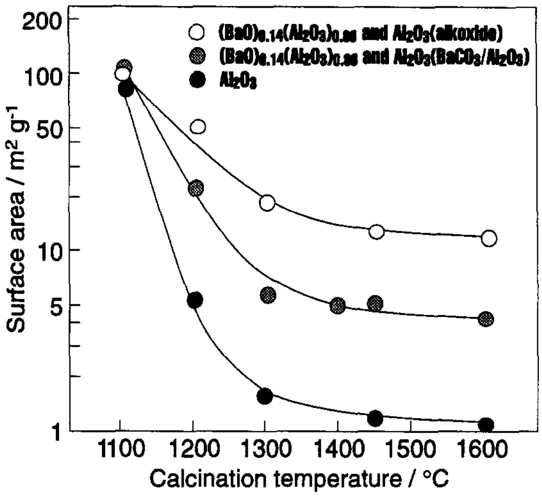


Fig. 5. Temperature dependence of surface areas of $(BaO)_{0.14}(Al_2O_3)_{0.86}$ and Al_2O_3.

3.2. Analysis of sintering behavior of hexaaluminate

A series of hexaaluminate compounds crystallize in β-alumina or magnetoplumbite structure. Both of these structures consist of alternative stacking of a spinel block and a mirror plane along the c direction. A closed packing layer of oxygen is located in the spinel block, however the packing in the mirror plane and along the c direction is relatively loose. These two crystal structures, being different in the coordination of mirror plane, are regarded as hexagonal layered structures. The anisotropic nature of this crystal strongly affects the kinetics of crystal growth and diffusion, as explained below.

The electron microscopic analysis revealed that the hexaaluminate powder prepared by hydrolysis of the alkoxides crystallized in platelike

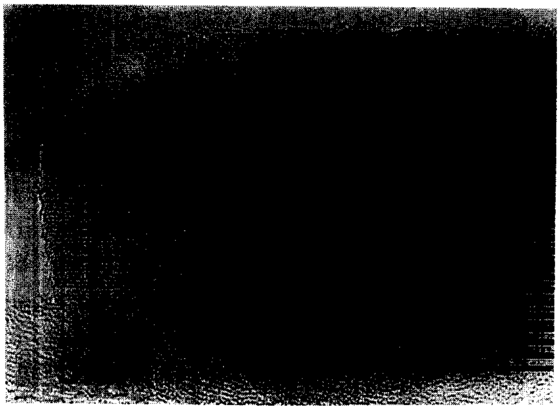


Fig. 6. TEM photograph of $Sr_{0.8}La_{0.2}MnAl_{11}O_{19-\alpha}$ calcined at 1300°C.

microcrystals. The size of the powder is 30 nm in thickness and 200 nm in diameter. The plate-like crystals were also observed for the sample derived from powder mixture; however the sample contains granular-shaped and amorphous crystals. The granular and amorphous crystals observed in the calcined powder mixture are the unreacted particle or intermediate phases. The composition among the micro-crystal is not uniform in the sample from the powder mixture. The high resolution image was obtained for the crystal from the alkoxides process (Fig. 6). The layered structure was obvious from the high resolution image observed from the parallel direction to the basal plane of the microcrystal. The high resolution image from the basal plane indicated the hexagonal structure of this crystal. The crystals was grown to the kinetically favorable direction which is normal to (001), but the growth along this direction is thermodynamically unfavorable since deviation of aspect ratio from unity results in the large surface energy.

High thermal resistance of this series of compounds appears to be strongly related with this anisotropic bulk diffusion [6]. The mass transfer rate along the *c* direction is very slow as mentioned, but the crystal growth to the *a* or *b* direction is also unfavorable because it accompanies the increase in surface energy. The stable high surface area, therefore, is common property for the series of hexaaluminate which crystallizes in magnetoplumbite and β-alumina structures. The surface area after heating at elevated temperatures is dependent on the kind of *A* site cations and their substitution in these structures. The highest sintering resistance at elevated temperatures could be attained by $Sr_{0.8}La_{0.2}Al_{12}O_{19.1}$. Mn-substituted Sr–La hexaaluminate is, therefore, used for the practical application to high temperature combustion.

4. The active component for combustion reaction

For low and medium temperature combustion, precious metal and transition metal perovskite-type oxides were known as active species. The activities of oxidation reaction for single oxide catalysts have been reported to follow the volcano-shaped pattern versus the heat of oxide formation. The activity is maximum for a precious metal catalyst generally, but decreases with either increasing or decreasing heat of oxide formation, $-\Delta H_f^0$. the metals with low heat of formation are inactive for adsorption of oxygen. As for the metals with high heat for oxide formation, bonding between metal and oxygen is too strong to be used for the combustion reaction. The activity of high temperature combustion also appears to obey this relationship, but the summit of volcano is expected to shift to high $-\Delta H_f^0$ side as compared with the low temperature reaction since the bonding between metal and oxygen is weakened with a rise in temperature.

For the hexaaluminate compounds with Ba or Sr, Mn is revealed to be most active for the combustion reaction. The Mn ions are substituted for the Al sites in the hexaaluminate lattice. Fig. 7 shows the volcano for the cation substituted Ba-hexaaluminate, $BaMAl_{11}O_{19-\alpha}$ for combustion of methane which is plotted vs. the enthalpy for formation of single oxide $MO_{1.5}$ from MO. The Mn-substituted hexaaluminate is located at the summit. The metals in the left foot region favor the divalent state in the hexaa-

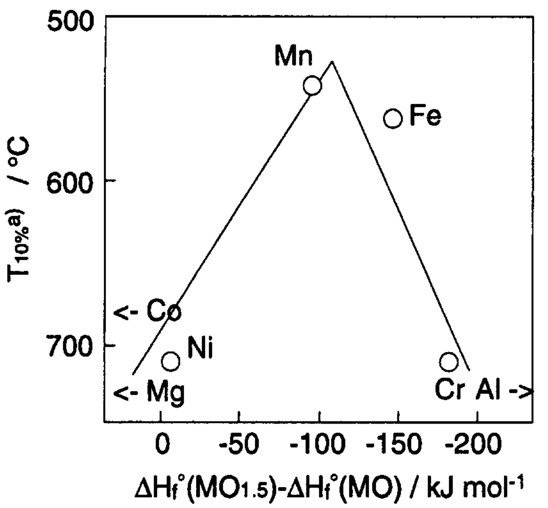


Fig. 7. Correlation of the catalytic activity with $\Delta H_f^0(MO_{1.5}) - \Delta H_f^0(MO)$ in CH_4 oxidation. (a) Temperature at which conversion level is 10%. Reaction condition; CH_4, 1 vol.-%; air, 99 vol.-%; SV, 48000 h^{-1}.

luminate lattice, whereas those in right foot region are in trivalent state. Only in the case of Mn and Fe, the cations are in mixed valence state of 3 + and 2 + [4].

5. Activity of Pd catalyst for methane combustion

Palladium catalysts have been most popularly employed as combustion catalysts of natural gas. As for the catalytic combustor for gas turbines, they are used for the initiator of hybrid combustion or the front zone catalyst of the series arranged honeycombs, since their quite low light off temperature is very attractive. The catalytic activity of cation-doped hexaaluminate was not so high as Pd catalyst or some perovskite-type oxides. But the thermal stability is superior for hexaaluminate to the Pd or perovskite-based catalysts. Pd/cordierite is the popular combustion catalyst due to its very high thermal shock resistance resulting from the low thermal expansion of the support material. However, the thermal stabilities are not high enough due to its low melting point.

We have investigated Pd-supported hexaaluminate and alumina based catalysts for methane combustion [7]. The surface area of hexaaliuminate is generally smaller in exchange for the better thermal stability than the alumina catalyst, so the ignition temperature for Pd/ hexaaluminate was higher than Pd/Al_2O_3 due to poor dispersion of palladium. However, modification of catalytic activity is possible by selecting the component cations in the mixed oxide support. The temperature dependence of Pd/SLA (SLA: $Sr_{0.8}La_{0.2}Al_{11}O_{19.1}$) and Pd/SLMA are shown in Fig. 8. The oxidation of methane started from ca. 300°C. The activity of Pd/SLA rose up sharply below 700°C, however at 700°C the slope of the activity curve turned to negative. The activity decrease was revealed to be related with the oxidation state of Pd. The oxidized state of Pd, i.e., PdO, is more active than the metallic state of Pd. Although the activity abruptly drops with the phase transition from PdO to Pd, the activity of metallic Pd also increased at higher temperatures. To apply Pd to the combustion catalyst such unstable behavior has to be taken into account depending on the reaction condition. In the case of Pd supported on SLMA, however the activity increased smoothly and monotonously with increasing temperature. The activity at low temperatures should be determined by Pd, whereas

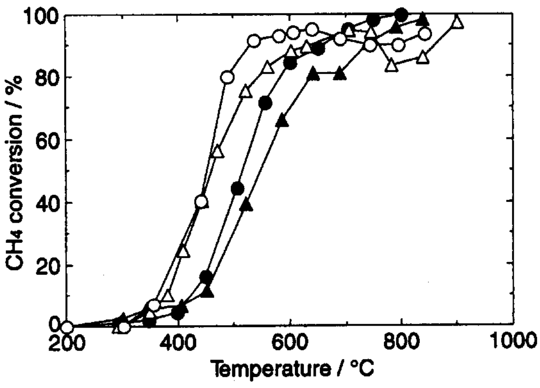


Fig. 8. Catalytic combustion of methane over Pd/SLA and Pd/SLMA. ○ Pd/SLA calcined at 1000°C; △ Pd/SLA calcined at 1200°C; ● Pd/SLMA calcined at 1000°C; ▲ Pd/SLMA calcined at 1200°C; Reaction condition; CH_4, 1 vol.-%; air, 99 vol.-%; SV; 48000 h^{-1}.

Table 2
Surface areas and catalytic activity over Pd (1.1 wt.-%)/Al_2O_3-*M*O calcined at 800°C

M	Surface area /m^2 g^{-1}	Catalytic activity [a]			
		T10	T30	T70	T90
-	139.3	340	370	420	500
Co	30.0	340	390	500	700
Cr	33.4	420	500	580	680
Cu	20.6	470	530	600	680
Fe	13.3	460	540	740	900
Mn	16.3	430	520	630	750
Ni	63.9	310	370	440	510

[a] Temperature at which conversion level is 10%, 30%, 70% and 90%, respectively. Reaction condition; CH_4, 1 vol.-%; air, 99 vol.-%; SV, 48000 h^{-1}.

that at high temperatures is governed by the hexaaluminate support. This behavior of Pd and Mn-substituted hexaaluminate implies that base metal oxides are more efficient at high temperatures as compared with precious metal catalysts.

Another important aspect of the Pd for combustion catalyst is to maintain high dispersion of metal oxide on the support. The activity of PdO quite depends on the surface area of metal. The kind of support strongly affects the oxidation activity of the Pd catalyst through the dispersion of Pd. The additive effect of transition metal oxide to alumina support is summarized in Table 2. The addition of the transition metal oxides always led to a decrease in surface area, therefore the catalytic activity is lowered with this addition in most cases. Addition of Ni to alumina also accompanies the decrease in surface area, but the activity was almost the same as the case of Pd/Al_2O_3. It has been revealed from the X-ray line broadening analysis that the dispersion of Pd is quite high on $NiO-Al_2O_3$ support.

6. Application of catalytic combustion to gas turbine

Recently, some groups are reported on the application of catalytic combustion to gas turbines [8,9]. These studies accelerate the research for practical application to clean and efficient combustors. Most of the catalytic combustors for gas turbine adopt hybrid combustion of heterogeneous catalytic reaction and homogeneous gas phase reaction. The relative contribution of two processes is different depending on the researchers. The catalytic reaction is used for the ignition and stabilization of combustion and, to attain high combustion efficiency, the rapid increase in conversion for homogeneous reaction is desirable. One typical construction of catalytic combustor is shown in Fig. 9 [8]. The catalyst is used to heat up the gaseous mixture and pre-mixed unburned fuel and combustion gas was then reacted by homogeneous reaction. This design limits the maximum temperature of the catalyst zone and therefore the catalyst deactivation by high temperature is minimized. High combustion efficiency and low emission of NO_x was attained.

The hexaaluminate so far mentioned was employed for the test apparatus for 160 kW prototype combustor gas turbine by cooperative work of Kobe Steel, Osaka Gas, and Catal. Chem. Inc., Far East (Fig. 10) [9]. The combustor consisted of 7 series arranged catalyst honeycombs with different activities and thermal stabilities depending on the temperature and conversion level at each location. Precious metals carrying cordierite honeycombs were set in the front zone. The temperature in this zone A–C is below 800°C in the operation condition but the

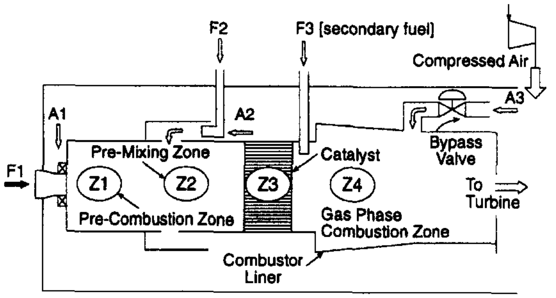
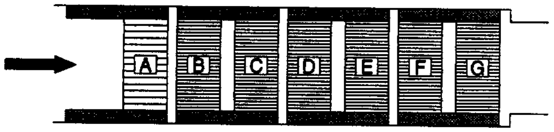


Fig. 9. Schematic illustration of hybrid catalytic combustor [8]. Z1, pre-heating zone; Z2, mixing zone; Z3, honeycomb catalyst; Z4, gas phase combustion zone; A1–A4, air inlet; F1–F3, fuel inlet.



	Catalyst	Cell number	Honeycomb length(mm)
A	Pd/Al_2O_3/Cordierite	200/in^2	20
B,C,D,E	$Sr_{0.8}La_{0.2}MnAl_{11}O_{19}$	300/in^2	20 x 4
F,G	$Sr_{0.8}La_{0.2}MnAl_{11}O_{19}$	300/in^2	20 x 2

Fig. 10. Schematic illustration of catalytic combustor using hexaaluminate catalysts [9].

high activity is necessary to initiate the combustion. The middle and back zone catalysts were hexaaluminate honeycombs. The series arranged structure was employed to avoid the crack of honeycomb due to the longitudinal temperature gradient. It was also proposed for relieving the radial thermal stress that each columnar honeycombs were cut into segmented sectors. The reaction temperature rises up from the inlet to outlet monotonously. In the down stream region, high thermal stability becomes the more important property rather than catalytic activity. The honeycombs heated at different calcination temperature were used to achieve this purpose. The final temperature at the outlet zone G reached to 1200°C. The combustion efficiency higher than 99% and NO_x emission less than 40 ppm are maintained at a catalyst outlet temperature of around 1000°C. To achieve high combustion efficiency, the control of catalytic activity and conversion at each reaction zone is necessary.

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