

Research and development on high temperature catalytic combustion

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Abstract

The history of high temperature catalytic combustion is introduced. Practical applications, some concepts to be considered, and lots of issues for realization of ideal complete systems for high-temperature catalytic combustion are discussed. Particularly, examples of catalyst supports with thermal stability, and new combustion catalysts, substitute hexaaluminates, are presented.

Keywords: Combustion; High temperature combustion

1. Introduction

Today, lots of the world's energy needed for the thermal power generation depends on the combustion of fossil fuels. On the other hand, these combustion systems have raised much of the problems of environmental disruption. One of the emission gases of the most serious concerns is nitrogen oxides (NO_x), which cause acid rain and resulting forest damage, and has become a hot issue in the world. Carbon dioxide leading to the greenhouse effect is another big target of the environmental protection and will not be reduced as long as we use fossil fuels at the current pace. In this circumstance, improving energy efficiency will be one possible way to reduce the emission of carbon dioxide.

To settle these global environment and energy issues, the combustion systems need to be much

improved for high efficiency and low pollutant emissions. Catalytic combustion has been proposed by Pfefferle and Pfefferle and developed as a method of promoting efficient combustion of lean fuel-air mixture with a minimum pollutant formation at low temperature as compared to conventional flame combustion. Catalytic combustion is applicable to gas turbines, boilers, aircraft afterburners, heat extraction, domestic heaters, etc. The term, catalytic combustion, generally means complete oxidation of fuels over solid catalysts regardless of the chemical reaction mechanism. But, purely catalytic processes cannot solely achieve the high performance required for commercial combustors. A possible process for attaining these objectives is 'catalytically supported thermal reaction', which achieves exceptional performance due to a design concept combining the features of both catalytic oxidation and homogeneous gas phase combustion [1].

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The use of an oxidation catalyst in gas turbines has been an important subject in the studies of catalysts and combustion since the 1970's, particularly in the USA. To date, there have been five international workshops, many technical papers and review articles devoted to catalytically stabilized thermal combustion [1–3]. These studies involved a number of catalyst materials, catalyst systems, modeling, and applications. With regard to the high temperature applications such as gas turbines, while preliminary results have been quite promising, there are some problems remained to be solved prior to the practical application. Firstly, the catalyst materials with the sufficient heat resistance have not been developed. The catalytic combustion will be operated in the range of 1000–1400°C. Conventional oxidation catalysts, such as supported palladium or platinum metals or simple metal oxides, are not resistant to these high temperature conditions. Secondly, the catalytic combustion mechanism is not well understood because of the complex interaction between heat and mass transfer and elemental reactions. The elucidation of the combustion mechanism is necessary for the optimal combustor design. This issue, particularly, picks up the reports which focus on the recent R&D of the high temperature catalyst materials modeling and the application for gas turbine systems with high temperature catalytic combustion in the International Workshop on Catalytic Combustion in 1994 in Tokyo.

2. Applications

Many practical applications to power generation, gas turbines, boilers and aircraft jet engines were investigated as a US National project from 1976 to 1981. Also in Japan, work in this field has been started at the later 70's. After the middle 80's, research and development in the US and Japan have been directed to the application to the LNG cycle combined with power generation and co-generation systems.

Typical concepts for the high temperature combustion system are classified as follows: (a) Com-

plete catalytic combustion (Fig. 1), (b) combined system of both partial catalytic combustion and flame combustion (Fig. 2A (II), Fig. 2B), and (c) combined system of both partially loaded catalytic combustion and flame combustion (Fig. 2A (I)).

In complete catalytic combustion, entire fuel is supplied to the catalyst bed where complete oxidation takes place. The combined system of both partial catalytic combustion and flame combustion also supplies the entire fuel to the catalyst. But, supplied fuel is consumed partially in the catalyst bed to increase the gas temperature. The residual fuel ignites flame combustion in the section downstream of the catalyst bed or in a main combustion chamber located downstream of the catalyst bed. On the other hand, fuel is separately supplied into the catalyst bed and downstream of

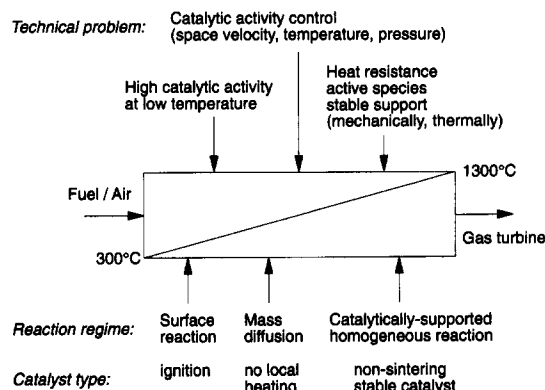


Fig. 1. The factors for ideal complete catalytic combustion.

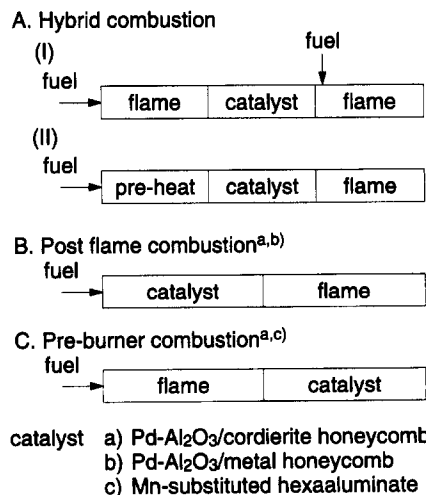


Fig. 2. Proposed catalytic combustor types.

the catalyst bed in the combined system of both partially loaded catalytic combustion and flame combustion. Secondary fuel introduced downstream of the catalyst bed ignites flame combustion.

Ideal complete catalytic combustion for gas turbine combustors is schematically illustrated in Fig. 1, which schematically shows an axial temperature profile in a catalyst bed. In the front part of a catalyst bed, the rate of total reaction is determined by the surface reaction on the catalyst because the temperature is sufficiently low. This means that, in this region, high catalytic activity is strongly required to ignite combustion. After initiation of the surface reactions, the reaction rate increases rapidly with an increase in temperature so that the overall process become limited by the rate of mass diffusion. As the exothermic surface reaction proceeds further, the axial temperature increases and consequently, the gas phase reaction is initiated. As a result of this profile, a catalyst near the outlet seems to be exposed to extremely high temperature. Therefore, the catalyst located in this region must possess not only the catalytic activity to retain lean fuel combustion in the gas phase but also the thermal stability to suppress sintering.

There are three main problems to attain complete ideal catalytic combustion:

- High catalytic activity for the low ignition temperature.
- Temperature control for the appropriate thermal profile (no local heating and gradual temperature increase from inlet to outlet)
- High heat resistance of the catalyst concerning catalytic activity, surface area and thermal shock resistance

In particular, ignition of fuel/air mixtures at the lowest possible temperatures is required for the high temperature catalyst materials. If a new catalyst will be found, which will ignite at 250°C, a conventional preburner will not be needed and thus eliminating NO_x. The catalyst activity should be sufficiently appropriate to control thermal distribution without the hot spot from the lowest inlet temperature to the desirable outlet temperature.

The catalyst should have a large surface area, high thermal shock resistance, and catalytic activity in the final stage region for complete combustion as shown in Fig. 1.

On the other hand, the other two concepts (b and c) are based on the combination of catalytic and flame combustion. These hybrid concepts are profitable to reduce the thermal damage of catalyst materials because the maximum in the axial temperature will be located far from the catalyst bed. In these combined systems, one of the issues is to develop catalysts which have an important role. Other important issues are to optimize combustor components and sequential combustion control systems for practical application. Corresponding to these various concepts, several different types of catalytic combustors for gas turbines have been proposed as shown in Fig. 2.

3. Materials

The combustion catalysts operating at above 1 200°C require the high thermal stability as well as the catalytic activity. Even though this means that the properties of catalyst necessary for catalytic combustion are quite different from those for conventional oxidation catalysts, the catalyst design from such a viewpoint has not been examined so far. Combustion catalysts are generally comprised of active species, oxide supports and substrates. Substrates are shaped into monolithic honeycomb structure in order to reduce the pressure loss. The most common substrate is based on alumina, which is inexpensive and can be operated at high temperature (> 1480°C). Zirconia can be used at higher temperatures up to 2210°C without thermal deterioration. Cordierite is the most widely used honeycomb ceramic with the highest thermal shock resistance. However, the low melting point will limit the operation temperature below 1300°C. Aluminum titanate ceramics with low thermal expansion are studied as an alternative substrate for higher temperature applications.

Support and/or washcoat oxides play an important role even in catalytic combustion. One of the

Table 1
Examples of catalyst supports with thermal stability

Catalysts	T and weight	Ref.
Li, K, Mg-added activated alumina	ca. 600°C, 240 m ² /g	[4]
Ba-added γ -alumina	ca. 1200°C	[5]
Si-added γ -alumina	ca. 1200°C	[5]
La-added γ -alumina	1000°C, 120 m ² /g	[6–8]
Lanthanide (La,Pr,Nd)-added alumina	1150°C, 63 m ² /g	[10]
La-added γ -alumina	900°C, 92 m ² /g	[10]
La-added γ -alumina	1050°C, 0% H ₂ O, 51 m ² /g	[9]
	1050°C, 20% H ₂ O, 5 m ² /g	
Si-added γ -alumina	1220°C, 20% H ₂ O, 51 m ² /g	[15]
SiO ₂ -Al ₂ O ₃ , mullite	1400°C, 31 m ² /g	[12]
Zr, Ca, La, Th added alumina	Kinetic model of stabilization	[14]
Lanthanide-hexaaluminate	1200°C, 37 m ² /g	[17]
Alkaline earth-hexaaluminate	1600°C, 10 m ² /g	[18,19]

crucial problem is to suppress the sintering and to retain a large surface area of oxide supports. For transition aluminas, which are the most commonly used support material, the phase transformation to α -phase accompanies the significant loss in surface area. Thermal stabilization of alumina by additives has been reported by several researchers as summarized in Table 1 [4–16]. These effects are originated from the inhibition of the phase transformation to α -alumina and/or the sintering of metastable phase, which cause significant loss in the surface at above 1000°C. Lanthanum oxide, which is the best known inhibitor against the sintering of transition aluminas, produces a surface layer identified as LaAlO₃. Such a surface layer inhibits the surface diffusion of transition aluminas or nucleation of a alumina in the initial step of the phase transformation. Addition of SiO₂ also produces surface compounds (silanol groups) or glassy layers, which prevent the phase transformation. Other additives, such as Li, K, and Ba, are considered to suppress an atomic diffusion by occupying cation sites in the bulk.

A different type of thermal stabilization was reported on the higher temperature uses (> 1200°C). The addition of La₂O₃ or BaO to alumina are effective in retaining the surface area

as compared to pure alumina (Fig. 3) when the hexaaluminates with β -alumina or magnetoplumbite structures are produced as a result of solid state reactions [17–19]. Other rare earth elements (Pr, Nd) and/or alkaline earth elements (Ca, Sr) also show the same stabilization effect.

Noble metals possess the highest catalytic activity and thus initiate the catalytic oxidation of hydrocarbon fuels at the lowest possible temperatures. From a practical view point, however, the use of noble metals in a combustor should be limited because of the volatilization and the sintering at operation temperatures. Noble metals other than Pt and Pd can be hardly used for these reasons. Some transition metal oxides and/or their mixed oxides, such as the perovskite type, are well-known complete oxidation catalysts, of which activities are comparable to those of noble metals. But, these oxide materials are also easy to sinter above 1000°C. Recently, new combustion catalysts based on hexaaluminate have been developed by partial substitution of the Al site by Mn. Sr_{0.8}La_{0.2}MnAl₁₁O_{19- α} catalyst still had a surface area of 13 m²/g after 1 300°C for 5 h and a lifetime test the of catalytic activity carried out at 1 300°C in air for 1 year [20]. The non-sintered and the same composition catalyst for a long period is under investigation for practical application. The combustion performance of the substituted hexaaluminate shaped into a monolithic honeycomb are now investigated as thermally stable

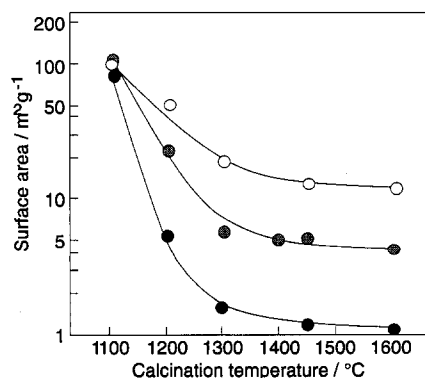


Fig. 3. Temperature dependence of the surface areas of (BaO)_{0.14}(Al₂O₃)_{0.86} and Al₂O₃, ○, (BaO)_{0.14}(Al₂O₃)_{0.86} (alkoxide), shaded ○, (BaO)_{0.14}(Al₂O₃)_{0.86} (BaCO₃/γ-Al₂O₃); ●, Al₂O₃.

catalysts for the high temperature catalytic combustion [21].

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