ELSEVIER

Catalysis Today 35 (1997) 129–135

CATALYSIS TODAY

Catalytic combustion gas turbine systems: the preferred technology for low emissions electric power production and co-generation

Ralph A. Dalla Betta

Catalytica, Inc., 430 Ferguson Drive, Mountain View, CA 94043, USA

Abstract

The operating requirements for practical catalytic combustion systems are presented. Catalytic materials for methane combustion are then reviewed in light of these operating requirements. Measured catalytic rates for methane oxidization for a number of active metal and oxide catalyst systems are reported and compared. The precious metals, particularly Pd, are most active. The oxides can exhibit high surface areas but in all cases have a much lower areal activity resulting in a substantially lower weight specific activity. Data on the thermal stability and volatility of both support and active components are presented and discussed in terms of the required operating temperatures. It is concluded that at the required operating temperature for modern gas turbines, most catalyst systems would not have sufficient stability and life. An alternative approach is to limit the catalyst temperature and to react a portion of the fuel after the catalyst. This process has substantial advantages. This latter system will be described and the important catalyst performance characteristics discussed. Test results demonstrate NO_x levels below 2 ppm even at combustor outlet temperatures as high as 1500°C.

Keywords: Combustion; Gas turbine systems; Low emissions electric power production

1. Introduction

In catalytic combustion, a combustible compound and oxygen react on the surface of a catalyst to completely oxidize the combustible compound. This process takes place without a flame at much lower temperatures than those present in conventional flame combustion. Due partly to this lower operating temperature, catalytic combustion produces lower emissions of nitrogen oxides (NO_x) than conventional combustion. Because of these lower NO_x emissions, there is a growing interest in applying this technology to power generation, particularly in gas turbine combustors.

Commercially available NO_x control technologies for gas turbines and other combustion processes includes water and steam injection, lean premixed combustion (LPM) and selective catalytic reduction (SCR). The first three approaches have shown the ability of reducing the NO_x emissions level to approximately 25 ppm while SCR can further reduce NO_x levels to 10 and even 5 ppm. Catalytic combustion has been shown to reduce NO_x to levels of 1 to 5 ppm depending on the gas turbine/combustor system. A comparison of costs of these technologies based on United States Environmental Protection Agency published actual commercial costs is shown in Fig. 1 [1]. The cost is ex-

PII S0920-5861(96)00139-3

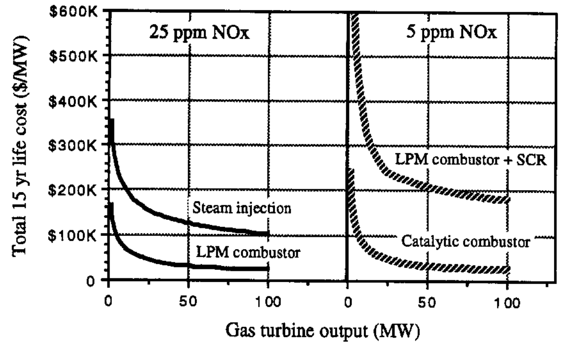

Fig. 1. Cost comparison of several NO_x control technologies for emissions levels of 25 and 5 ppm.

pressed as the net present value (NPV) per megawatt of engine output ($/MW) which is essentially the total cost including capital and operating cost over a 15 year period expressed as a current value assuming an 11% interest rate. The cost of NO_x control becomes very high for small engines due to the high capital cost. While LPM combustor technology has a moderate capital cost, it can only achieve ~ 25 ppm NO_x levels. SCR must be added to LPM to obtain levels of 5 ppm NO_x, greatly increasing the cost. For applications that require emissions levels below 5 ppm, catalytic combustion should be the lowest cost and preferred technology.

2. Performance requirements

A gas turbine consists of the following components:

Compressor: Compresses incoming air to a high pressure

Combustor: Adds fuel to the air and combusts this fuel to produce a hot high velocity gas stream

Drive turbine: Extracts work from the hot high velocity gas

This process results in two basic requirements for the catalytic combustion system. The inlet temperature to the catalyst is determined by compressive heating of the air in the compressor section. In addition, the catalyst should have sufficient catalytic activity at this temperature for the reaction of the fuel and oxygen. In addition, the combustor system must produce a gas at the outlet of the combustor that is at the temperature required by the gas turbine for efficient operation. The basic operating requirements for the catalyst system in most modern industrial and utility gas turbines are:

Inlet gas temperature	290 to > 500°C
Combustor outlet temperature	1000 to ~ 1500°C
Operating pressure	8 to 20 atm

The low end of the inlet temperature range requires that the catalyst has a very high activity. Since the major first application will be on natural gas fuelled engines, the catalyst activity requirement is for methane oxidation. The required high combustor outlet temperature for modern high efficiency engines requires that the catalyst be able to work at this high temperature or achieve this temperature by unique system design. As catalyst performance characteristics are discussed below, these operating requirements will be very important.

3. Stability of catalytic materials

3.1. *Activity of catalytic materials*

A wide variety of materials have been investigated for methane oxidation in excess oxygen. The work covers all of the precious metals and numerous oxides. A compilation of some of the more active and stable catalysts are summarized in Table 1, where the specific activity per gram and areal rates are tabulated. The reaction rates were measured in a single pass flow reactor with 2% methane in air at 1 atm pressure, as described previously [2]. The surface area of the oxides were measured by the standard BET method and the Pd and Pt surface areas were measured by H_2–O_2 titration as described previously [3].

The precious metals show the highest reaction rate per unit metal surface area (areal rate)

Table 1
Comparison of methane oxidation rate on some metals and oxides. At 400°C in 2% methane in air at 1 atm pressure

Material	Areal rate (10^{-7} mol $m^{-2}\,s^{-1}$)	Surface area at ~1000°C (m^2/g)	Specific rate (10^{-7} mol $g^{-1}\,s^{-1}$)
Pd/Al_2O_3	140	2	300
Pt/Al_2O_3	50	1	50
Co_3O_4	4.4	3	1
$LaCoO_3$	0.36	3	1
$La_{0.5}Sr_{0.5}CoO_3$	1.2	6	7
$Cu/La-Al_2O_3$	0.09	80	7
$Sr_{0.8}La_{0.2}MnAl_{11}O_{19}$	0.045	70	3

and palladium is the most active catalyst. The most active oxide is Co_3O_4. Comparing Pd catalysts with Co_3O_4, Pd is more active by 30 fold. However, the interest in the oxides arises from the general perception that these materials are more stable and will generally show a higher surface area and per gram activity at high temperatures. For a catalyst contained in a gas turbine combustor, the per gram activity is the important measure because the extent of fuel conversion will be a function of the total catalyst activity contained within the combustor volume.

However, a review of the materials contained in Table 1 shows that the oxides do show somewhat higher surface areas but the increased surface areas do not compensate for the lower areal rate. Pd can be supported on an inert oxide such as Al_2O_3 or ZrO_2 to maintain a Pd surface area in the range of 1 m^2/g. However, Co_3O_4 has an areal rate 30 times lower than Pd but sinters easily so that only a low surface area is readily maintained. This is typical of perovskites and results in a group of materials that have a low activity compared to supported Pd catalysts. Lanthanum cobaltate and the strontium lanthanum cobaltate show similar low surface areas and low activities. Some research has concentrated on using refractory oxides as supports for the oxides to increase their dispersion and total exposed surface area. In all cases, the oxide is not adequately stabilized or reacts with the support material to form a compound of low catalytic activity.

The $Cu/La-Al_2O_3$ is a material that has been extensively studied because the La-stabilized alumina shows a high surface area. Doping with Cu imparts activity for methane oxidation and was developed as a high temperature catalytic combustion catalyst due to this combination of high surface area at high temperature and methane combustion activity [4,5]. As shown in Table 1, the $La-Al_2O_3$ shows a surface area of 80 m^2/g after thermal treatment at 1000°C. However, the areal activity is only 0.09×10^{-7} $mol\,m^{-2}\,s^{-1}$, resulting in a specific activity in the same range of the other oxides and substantially lower than the supported Pd catalysts. Similarly, the hexaluminates, such as $Sr_{0.8}La_{0.2}MnAl_{11}O_{19}$, have been developed as a group of oxide materials with stable surface areas at high temperature and which have good activity for methane oxidation. This particular substituted hexaluminate shows the highest per gram and areal activity of the group [6,7]. Again, similar to the other oxide materials, this oxide has a low areal activity, resulting in a low activity per gram when compared to Pd and Pt systems.

In general, these results suggest that supported precious metals particularly Pd will be the most active catalyst barring other phenomena such as vaporization or reaction of the active component with the support materials.

3.2. Support sintering

For precious metal catalysts or supported oxide catalyst materials, the surface area stability of the refractory oxide support is important. The surface area of several typical supports is presented in Fig. 2. At temperatures below 900°C, surface areas in the range of 100 m^2/g can be maintained on several materials. The hexaluminate appears to be the most thermally stable, retaining a surface area of 65 m^2/g at 1200°C. However, recent work shows that even these materials will sinter upon long exposure in a high water vapor environment with the surface area dropping from 20 to 5 m^2/g at 1300°C [8].

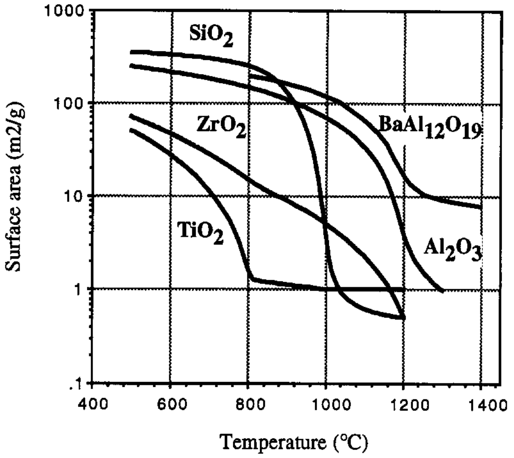

Fig. 2. Surface area of several support materials after calcination in air for 10 h.

Some of these support materials can be stabilized in a manner similar to the Ba-, La- or Si-stabilization of Al_2O_3 and this does increase the surface area that can be retained at temperatures in the range of 1100 to 1200°C, but it should be noted that the most modern turbines operate with combustor outlet temperatures of 1400 to 1500°C. Clearly, high support surface areas cannot be maintained for long periods at these very high temperatures. If a catalytic combustion technology is to be used for a broad range of turbines, then it must be applicable to these very high temperature ranges.

3.3. Vaporization of catalyst materials

While the volatility of the support material or the active catalytic components is not usually considered a problem, in the case of catalytic combustion at these very high temperatures volatilization must be considered an important factor. Vapor pressure data have been collated and remeasured in several cases and have been summarized recently by Hildenbrand and coworkers [9]. At temperatures of 1000 and 1400°C, the vapor pressures of several catalytic materials are collected in Table 2. These vapor pressures are reported for an atmosphere of 50% H_2O and 50% O_2 since in most cases the volatile species are oxides and hydroxy oxides. In the case of the catalytic elements, copper and cobalt are especially volatile. At 1400°C, the vapor pressure of the copper oxides would be approximately 1.3 kPa (10 Torr). Pt and Pd are significantly less volatile then copper or cobalt but do have significant vapor pressures at temperatures of 1000°C and above. It may be surprising to note that platinum is more volatile than palladium. Assuming that loss of material from a catalyst is a diffusion controlled process, the loss of Pt from a monolithic catalyst system operating at 1000°C is shown in Fig. 3. At this catalyst temperature, the predicted loss of platinum is so rapid that 70% of the metal is lost in 15 h of operation. Clearly, platinum cannot be used in the range of 1000°C or higher and be expected to have a significant operating life. Similarly, some support components are also volatile. Of particular interest are barium and silica which are used as stabilizing additives for alumina supports. In addition, at 1400°C even alumina would be somewhat volatile.

Of course, these materials can be stabilized toward volatilization by reaction with other materials to produce a compound that has a lower vapor pressure. An example would be RuO_2 which forms the highly volatile RuO_4 in oxygen at high temperature. Reaction of the RuO_2 with

Table 2
Vapor pressure of selected catalytic and support elements in equimolar H_2O/O_2 mixture at 1 atm

Element	Vapor pressure (atm)	
	at 1000°C	at 1400°C
Catalytic components		
Cu	5.6×10^{-4}	1.3×10^{-2}
Co	2.8×10^{-6}	1.6×10^{-4}
Mn	1.6×10^{-7}	7.9×10^{-5}
Pt	3.5×10^{-7}	2.0×10^{-5}
Pd	3.2×10^{-9}	5.6×10^{-6}
Support components		
Ba	1.8×10^{-4}	5.0×10^{-3}
Cr	1.8×10^{-5}	1.0×10^{-4}
Si	5.0×10^{-7}	7.9×10^{-5}
Al	3.5×10^{-9}	2.8×10^{-7}
Ti		2×10^{-10}

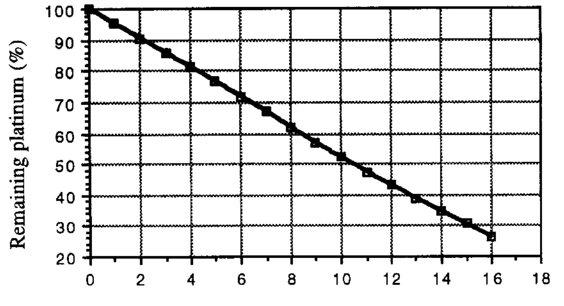

Fig. 3. Predicted loss of platinum from 1% Pt monolithic catalyst operating at 1000°C in air and H_2O.

BaO produces $BaRuO_3$ that has a vapor pressure that has been estimated to be 10^6 times lower and thus greatly reduces vaporization losses at high operating temperatures [10]. However, reaction of the catalytically active element will generally produce a compound with substantially lower catalytic activity. An example is the reaction of active Co_3O_4 with alumina to form surface or bulk cobalt aluminates. The Co_3O_4 is very active, but the supported Co catalyst treated at temperatures of 850 to 900°C is less active by more than 100 fold [11].

3.4. Required catalytic activity

As mentioned in Section 2 above, it is desirable to have sufficient catalytic activity at the catalytic combustion catalyst inlet to react methane and oxygen at the air temperature from the gas turbine compressor since this is the region of lowest temperature for the catalyst. This temperature, which depends on the pressure ratio of the gas turbine engine, can be as low as 290°C. The catalyst must be able to "light-off", that is, have sufficient methane oxidation activity to exceed the heat transfer at the catalyst surface and cause the catalyst substrate temperature to rise substantially above the gas temperature. A typical light-off or ignition test result is shown in Fig. 4. These tests were done in a full pressure, full flow sub scale catalytic combustion reactor that has been described previously [12]. In this case, a supported palladium catalyst was coated onto a corrugated metal honeycomb monolithic structure of 50 mm diameter and placed in the flow path of the combustion reactor. Air and ~ 4% methane are flowed at 9300 standard liters per minute (SLPM) at a pressure of 11 atm. The temperature of this mixture is slowly increased and the outlet gas temperature from the catalyst is monitored. Fig. 4 shows that for increasing temperatures, the catalyst begins to react significant methane at 410°C and has reached its fully ignited state at 420°C inlet temperature. Upon decreasing the temperature, the catalyst does not begin to lose activity until the temperature is below 360°C.

In previously published work, a series of catalysts were measured for ignition performance at high pressure, then the washcoat layer was removed and the specific activity measured in a differential reactor. A very good correlation was found between the ignition temperature and the washcoat specific activity [13]. Thus, the optimum performance of a catalytic combustion catalyst will be obtained with a very high activity catalyst at the catalyst inlet where the gas temperature is the lowest. However, maintenance of a high activity is made more difficult by the fact that these combustion catalysts operate at very high temperature resulting in sintering and loss of catalyst activity.

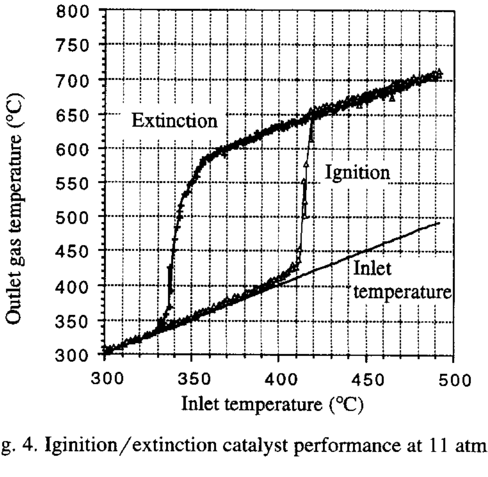

Fig. 4. Iginition/extinction catalyst performance at 11 atm.

4. Catalytic combustion system

4.1. Temperature limited catalytic combustion system design

One approach to the design of a catalytic combustion catalyst system is to limit the catalyst temperature and then to complete the combustion of fuel just downstream of the catalyst. This system has been described previously and is shown schematically in Fig. 5 [12]. In this design approach, the catalyst is divided into several stages, with each stage designed to perform a specific function. The properties of the catalyst coating for each stage can then be designed to emphasize the performance required for that particular stage. A second aspect of this system design is that the catalyst is designed to limit the maximum catalyst operating temperature.

4.2. Inlet stage

This stage is designed with a very high catalytic activity. This would require that the catalyst maintain a high surface area and high dispersion of the catalytic element. In general, this stage consists of Pd based catalysts on high surface area supports. In addition, the operating temperature of this stage is limited to a relatively low value in order to stabilize this high surface area and activity.

4.3. Outlet stage

Subsequent stages will have a substantially higher inlet gas temperature due the partial reaction of fuel over the inlet stage catalyst and thus will require only sufficient activity to operate at this temperature. This stage also operates at a higher temperature so that it can produce the required outlet gas temperature necessary to initiate the homogeneous combustion process.

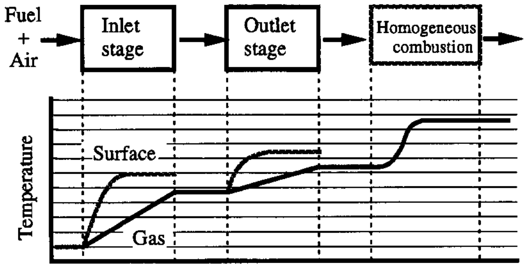

Fig. 5. Schematic diagram of low NO_x catalytic combustion system.

4.4. Homogenous combustion

As the hot gases containing significant unburned fuel leave the catalyst, a homogeneous combustion process is initiated that burns the remainder of the fuel and produces the high gas temperature required by modern gas turbines.

There are numerous advantages to this design approach. Limiting the temperature of the catalyst results in stable very high activity catalyst materials that give improved performance and longer catalyst life. The combustion of a portion of the fuel downstream of the catalyst overcomes the thermal sintering and vaporization problems described in Section 3 above. Typical system designs limit the catalyst temperature to 700–950°C, virtually eliminating the vaporization problem and allowing the use of very high activity catalysts at the inlet stage.

4.5. Performance results

Control of NO_x is the primary objective driving the development of catalytic combustion. The NO_x levels obtained in sub scale tests employing the staged system design are shown in Fig. 6. These results were obtained with natural gas fuel and air at the pressures and combustor outlet temperatures shown. At combustor temperatures as high as 1500°C, the NO_x level was 2.2 ppm. In all of these test runs, the CO and unburned hydrocarbon (UHC) levels were below 5 ppm and were typically less than 2 ppm. In all of these tests, the catalyst operating temperature was in the range of 850 to 950°C, substantially lower than the combustor outlet temperature.

In general, the CO and UHC emission levels are controlled by the temperature in the post

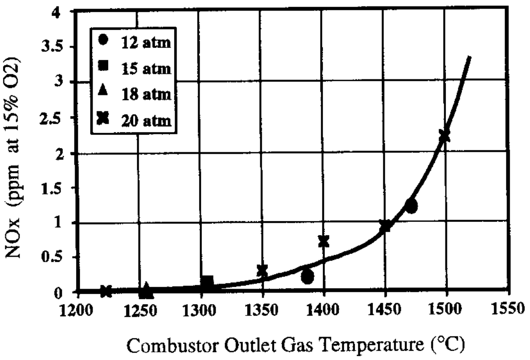

Fig. 6. NO_x emissions from a staged catalytic combustion system operated at combustor outlet temperatures from 1225 to 1500°C and pressure from 12 to 20 atm.

catalyst zone and at combustor outlet temperatures of 1200°C and higher, the CO and UHC levels are below 5 ppm. Even though the post catalyst temperature should be above 1200°C to burn away remaining fuel and CO, the turbine inlet temperature can be substantially lower by bypassing compressor air and adding this as a diluent downstream of the homogeneous combustion zone.

In summary, the demonstrated performance of this catalytic combustion system is:

Homogeneous combustion zone temperature	1200 to 1500°C
Combustor outlet temperature	900 to 1500°C
Catalyst inlet temperature	360 to 650°C
Pressure	3.8 to 20 atm
Emissions (at 15% O_2)	
NO_x	< 1 to 2.5 ppm
CO	< 5 ppm
UHC	< 5 ppm

Work is currently in progress to incorporate this catalytic combustion system in an operating gas turbine engine and to demonstrate long term durability.

References

[1] US Environmental Protection Agency report, EPA-453/R-93-007 (1993).
[2] F.H. Ribeiro, M. Chow and R.A. Dalla Betta, J. Catal., 146 (1994) 537.
[3] J.E. Bensen, H.S. Hwang and M. Boudart, J. Catal., 30 (1973) 146.
[4] I.I.M. Tijburg, Preparation and Properties of Thermostable Alumina-supported Copper Catalysts, Thesis, State University of Utrecht, The Netherlands, 1989.
[5] M.C. Marion, E. Garbowski and M. Primet, J. Chem. Soc. Faraday Trans., 87 (1991) 1795.
[6] M. Machida, K. Eguchi and H. Arai, J. Catal., 120 (1989) 377.
[7] M. Machida, K. Eguchi and H. Arai, J. Catal., 123 (1990) 477.
[8] H. Sadamori, Proc. Int. Workshop on Catalytic Combustion of Natural Gas, SRI International, 1992.
[9] D.L. Hildenbrand, K-H. Lau and J.G. McCarty, Gas Research Institute Report GRI-92/0521, November 1992.
[10] M. Shelef and H.S. Gandhi, Plat. Met. Rev., 18 (1974) 2.
[11] Y.F.Y. Yao and J.T. Kummer, J. Catal., 46 (1977) 388.
[12] R.A. Dalla Betta, J.C. Schlatter, S.G. Nickolas, D.K. Yee and T. Shoji, ASME 94-GT-250, Int. Gas Turbine Congress, The Hague, The Netherlands, 1994.
[13] R.A. Dalla Betta, Catal. Today, 26 (1995) 329.