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Monoliths in catalytic oxidation

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Abstract

Catalytic combustion is useful to avoid emission of nitrogen oxides, to combust fuel gas of different calorific levels, and to combust low contents of badly smelling or hazardous gaseous compounds. After dealing with some characteristics of catalytic combustion it is argued that catalytic combustion to a final temperature lower than about 800°C calls for a rapid transport of thermal energy out of the reactor. A fluidized bed in which combustion has been successfully performed is dealt with as well as a reactor filled with metal bodies sintered to each other and to the wall of the reactor. To achieve a sufficiently high catalytically active surface area a thin layer of silicone rubber is applied to the surface of the metal bodies and subsequently pyrolyzed to a highly porous layer of silica. To raise the thermostability alumina can be added to the silica layer.

To establish a final temperature above 900°C the homogeneous gas-phase combustion can be ignited by a solid catalyst or the reaction can be performed completely catalytically. Since the combustion reaction proceeds very rapidly at elevated temperatures, a large gas flow can be utilized, which calls for a reactor exhibiting a low-pressure drop. For catalytic combustion monoliths and gauzes are appropriate. The chemical composition of ceramic and metallic monoliths is dealt with as well as the cell densities and wall thicknesses of commercial monoliths. The application of active components to the surface of the walls of monoliths is subsequently discussed. Since monoliths do not allow radial mixing, a homogeneous gas mixture has to be fed to the monolith to prevent very high temperature levels moving randomly over the channels of the monolith and deactivating the catalyst.

With monoliths in gas turbines often catalytic ignition is used. To limit the temperature a fraction of the fuel feed is injected into the homogeneous combustion chamber. A number of alternatives of transporting the fresh fuel to the homogeneous combustion zone is mentioned. The cause of the catalyst temperature being higher than that of the gas flow is dealt with as well as the low volatility at elevated temperatures required for the catalytic components. Selection of the catalytically active materials is discussed and the procedure to bring the gas flow at the light-off temperature of the catalyst.

Monolithic combustors used in radiant heaters display often an oscillatory behavior. After dealing with the cause of the oscillations, prevention by means of a flame arrestor is mentioned.

Keywords: Monolith; Gas turbines; Catalytic oxidation; Radiant heater

1. Introduction

Since conventional burners have already been used for a very long period of time, a large body of know-how about their design and construction is available. Conventional burners are therefore very well optimized. However, conventional burners are based upon homogeneous gas-phase reactions, which are difficult to control resulting in the emission of nitrogen oxides, unburned hydrocarbons, and carbon monoxide. The main incentive for catalytic combustion has thus been the abatement of environmental pollution. Catalytic

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combustion can also be useful with the utilization of fuel gases of different combustion properties, which calls for justification of conventional burners. Since diluted natural gas can be processed with catalytic combustion, it is interesting to mention that in North–West Europe large deposits of natural gas diluted with 50–60% of nitrogen are present. However, the present abundance of natural gas in Europe causes the combustion of diluted natural gas to be not very urgent. Finally catalytic combustion is very effective in the conversion of small amounts of badly smelling or poisonous gaseous compounds into less harmful gases, such as carbon dioxide, water, and sulfur dioxide. Since the oxidation of the undesired compounds can be catalytically achieved at substantially lower temperature levels, complete oxidation can be performed economically.

The final temperature level to be achieved dominates the build up of a catalytic combustion reactor. Conventional catalysts can withstand temperatures of about 800°C without exhibiting a rapid deactivation. Temperatures up to about 800°C therefore can be obtained readily with catalytic combustion provided the thermal energy released can be transported sufficiently rapidly and efficiently out of the catalyst structure. Catalytic reactors displaying a rapid transport of thermal energy out of the catalyst structure will be dealt with in this review. When more elevated temperatures are desired, the demands on the catalysts are much more severe. Two different configurations can be envisioned. A catalyst in front of a homogeneous combustion zone can ignite homogeneous gas-phase combustion or combustion can be performed completely by catalytic reaction on a solid surface. The above two possibilities will also be considered.

Catalytic combustion calls for integration of the catalyst and the reactor, especially with final temperatures above about 800°C. When the pressure drop over the catalyst structure has, furthermore, to be limited, a special reactor configuration is a prerequisite. Monolithic reactors [1–4] and metal gauzes are structures that exhibit a low pressure drop. The abatement of air pollution by automobiles [5] has stimulated the development of monoliths. Monoliths are consequently attractive for catalytic combustion reactors exhibiting a low pressure drop. This review therefore will deal with the application of catalytically active components on the walls of monoliths.

Two applications of monolithic reactors in catalytic combustion will be reviewed more closely, viz., the utilization in gas turbines and in radiant heaters. Another obvious application for monolithic combustion reactors is the replacement of usual in-line burners to raise the temperature of gas flows that can accommodate carbon dioxide and water. Catalytic combustion with gas turbines has been studied already for a long period of time [6]. It will be argued that the development of a monolithic reactor suitable for gas turbines calls for accurate kinetic measurements together with reliable modeling [7]. Analogous demands involve the design of radiant heaters based on catalytic combustion.

2. Characteristics of catalytic combustion

Catalytic combustion [8–10] is characterized by a large heat of reaction, the adiabatic temperature rise is thus usually large, e.g., 1500°C. Adiabatic oxidation of 1% of methane in air roughly increases the temperature by 275°C. Methane–air mixtures ignite at methane contents from 5.3 to 15 vol% [12]. A methane content of 5.3 vol% corresponds theoretically to an adiabatic temperature rise of 1460°C. The rate at which the temperature rises within the catalyst bed depends also on the activation energy of the catalytic oxidation. The activation energy is much lower for gases, such as, hydrogen and carbon monoxide, than for gases, such as, methane. The activation energy for the oxidation of carbon monoxide on copper oxide, e.g., is 59 kJ/mol, while the corresponding value for the oxidation of methane is 101 kJ/mol as measured by Tijburg [11]. Hydrogen and carbon monoxide thus react with molecular oxygen on suitable catalysts, such as, platinum, already at low temperatures, e.g., at 70°C, whereas the catalytic oxidation of methane only sets on at temperatures of about 350°C. As a result the temperature increases very rapidly with the combustion of methane, whereas the temperature grows more smoothly with catalytic combustion of hydrogen or carbon monoxide.

The rate of combustion generally varies with the temperature as indicated in Fig. 1. At low temperatures the rate of the reaction is determined by the rate of the catalytic reaction proceeding on the surface of the catalyst. At higher temperatures the transport to

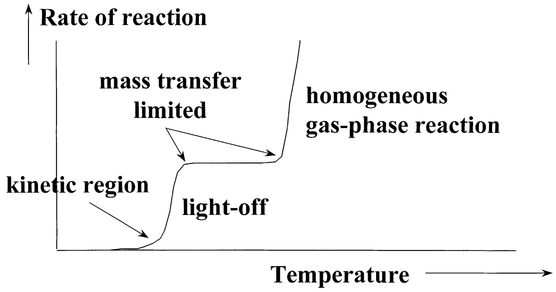

Fig. 1. Rate of catalytic oxidation as a function of temperature.

the catalytically active surface cannot keep up with the catalytic reaction. As a result the rate of the reaction is determined by the transport to the catalytically active surface, which increases much more slowly with the temperature than the catalytic reaction. At still higher temperatures the homogeneous gas-phase combustion sets on, which does not call for transport to a solid surface and thus can proceed very rapidly. At atmospheric pressure the homogeneous gas-phase reaction sets on at about 750°C, while the experimental evidence available indicates that at higher pressures the ignition temperature of the homogeneous gas-phase reaction is of the same order of magnitude.

3. Catalytic combustion below about 800°C

The most obvious catalytic reactor contains a fixed catalyst bed, which involves a stacking of porous catalyst bodies. To limit the pressure drop over the catalyst bed, the catalyst bodies must usually be larger than about 5 mm. The thermal conductivity of ceramic materials varies from about 0.8 to about 5 W/m K, while metals have a thermal conductivity of about 25 W/m K. The thermal conductivity of gases is still much lower, viz., 0.02–0.005 W/m K. The thermal conductivity of a porous solid therefore can approach that of gases provided the porosity is high. The thermal conductance of a stacking of porous catalyst bodies is low, viz., about 0.32 W/m K. In Table 1 the thermal conductances of fixed beds of bodies of different materials as mentioned by Boon [13] are summarized. As apparent from the data of Table 1 the thermal conductivity of the catalyst bodies is not determining the overall thermal conductance of the catalyst bed. The contacts between the catalyst bodies and, especially, between the catalyst bodies and the wall of the reactor are determining the overall thermal conductance.

Table 1
Heat conductivity of a stacking of bodies of different materials [13]

Material	Thermal conductivity (W/m K)
Alumina extrudates	0.32
Metal powder	0.53
Sintered metal powder	3–8

As a result the transport of thermal energy out of a usual fixed bed catalytic reactor proceeds slowly, which brings about that the temperature in the catalyst bed will rise to a level approaching that of the adiabatic temperature rise. At high fuel contents the catalyst will consequently rapidly deactivate. Usual fixed bed reactors are therefore only appropriate for catalytic combustion if fuel flows are processed so diluted that the adiabatic temperature rise leads to a final temperature lower than about 800°C. As a matter of fact the gas flow must be homogenized effectively to prevent volume elements having higher concentrations of fuel gas passing through the catalyst bed at randomly varying positions. The resulting locally high temperatures within the catalyst bed will deactivate the catalyst bed eventually completely.

With a fluidized bed the transport of thermal energy out of the reactor can proceed sufficiently rapidly to keep the temperature of the catalyst bed below about 800°C. Accordingly GasTec (Apeldoorn, Netherlands) was operating continuously a fluidized bed combustor of a diameter of about 2 m for about nine months using alumina bodies of about 1.0 mm as a catalyst support. The alumina was thermally stabilized by lanthanum oxide applied homogeneously over the alumina surface and the active component was copper(II) oxide, which was applied by impregnation of a copper(II) citrate solution [11]. The temperature of the catalyst bed could be readily maintained between about 550°C and 750°C. Coils within the fluidized bed were used to raise the temperature of an inert gas flow. The gas flow through the fluid bed was installed so that complete combustion of the fuel gas was achieved. Since the chemical process industry has a great need for thermal energy at a temperature level between about 350°C and 550°C, a fluid bed catalytic combustor offers interesting possibilities.

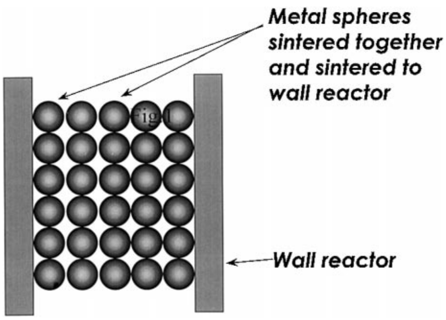

Fig. 2. Reactor containing a bed of sintered metal spheres.

When the desired flow of thermal energy is smaller or when transport of thermal energy by conduction is more favorable, a fixed bed reactor of a high thermal conductance is attractive. A fixed bed reactor of a high thermal conductance can be obtained by sintering metal bodies present within a metal tube by exposure to a gas flow containing hydrogen at an elevated temperature. Sintering leads to efficient thermal contacts between the metal bodies and between the bodies and the wall of the metal tube (Fig. 2). The dimension of the interstices between the metal bodies and, hence, the pressure drop of the resulting fixed bed reactor depends on the size distribution of the metal bodies used. With metal bodies of a size distribution exhibiting a low pressure drop, the surface area of the metal bodies is generally too low. As schematically indicated in Fig. 3, the surface area can be readily increased by applying a layer of silicone rubber on the metal bodies and subsequently pyrolyzing the rubber to a highly porous silica layer (surface area of the silica about 220 m^2/g) [14]. Addition of an aluminum compound to the silicone rubber can increase the thermal stability of the silica layer considerably; temperatures of about 1100°C do not lead to a significant drop in surface area. Applying a precursor of an active component on the surface of the porous silica layer leads to an active combustion catalyst structure. Van Looij et al. [14] have used a sintered metal reactor with platinum as the active component in the reaction of hydrogen with oxygen, while Mulder and Riphagen (GasTec) have conducted catalytic combustion of methane within a sintered metal reactor using palladium oxide as the catalytically active component. With both the reactors the temperature rise remained limited to at most about 50°C.

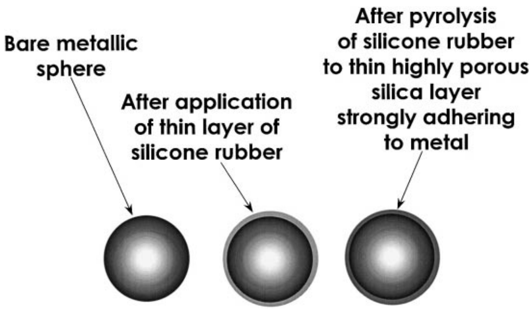

Fig. 3. Procedure to apply a highly porous silica layer strongly adhering to the metal by pyrolysis of silicone rubber.

4. Catalytic combustion with final temperatures above 900°C

As mentioned above catalytic combustion with final temperatures above 900°C can be performed in two ways, viz., catalytic ignition of the homogeneous gas-phase combustion reaction and completely catalytical oxidation. Catalytic ignition of the homogeneous gas-phase reaction is most obvious, since it is difficult to prevent the homogeneous gas-phase reaction to proceed at temperatures above about 800°C. To suppress the homogeneous gas-phase reaction, the radical intermediates of the homogeneous gas-phase oxidation have to be removed effectively by exposure to a sufficiently large surface area quenching the radicals.

At temperatures above about 600°C the catalytic combustion proceeds so rapidly that a small fixed bed reactor can be utilized. A small reactor can only deal with a relatively large gas flow if the pressure drop over the reactor is small. A low pressure drop can be achieved with a parallel flow reactor, a monolith, and a metal gauze. A parallel flow (parallel passage) reactor is schematically represented in Fig. 4. The catalyst is installed behind a screen leaving a central section that is empty and thus exhibits a low pressure drop. With catalytic combustion light-off of the catalytic reaction may require a fairly large catalytically active surface area. A radial flow reactor involving a modification of the parallel flow reactor, which is schematically represented in Fig. 5, can be suitable to light-off the catalytic combustion reaction. At higher temperatures the catalytic combustion proceeds so fast that the transport through long pores cannot keep up with

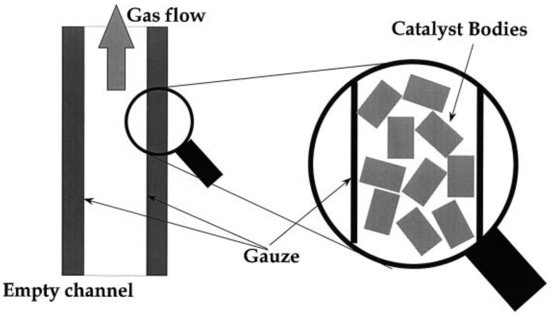

Fig. 4. Parallel flow reactor.

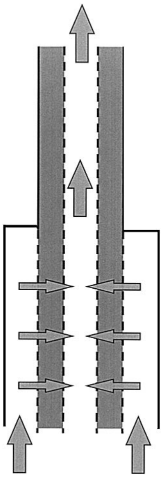

Fig. 5. Radial flow at the entrance of a parallel flow reactor.

the rate of the catalytic reaction. The fairly large catalyst bodies used in the parallel flow reactor are therefore not useful at higher temperatures.

Monoliths are extremely well suitable for catalytic combustion at high flow rates, since the pressure drop is very low. Furthermore, monolithic reactors are exposing a fairly large surface area to the gas flow. Fig. 6 schematically shows a monolith, a channel of a monolith, and a cross-section of the channel of a monolith on the wall of which a layer of catalyst has been applied. Catalyst layers of about 50 µm thickness are used; the thickness is usually not uniform, in the corners of the channels a thicker layer is often present. Since the pressure drop over a monolith is low, a high flow rate corresponding to Reynolds numbers of 300 000 or more can be used. With ignition of the homogeneous gas-phase reaction the final reaction in which the desired temperature above about 900°C is established proceeds behind the monolith in the homogeneous gas-phase. Below we will deal with the utilization of monoliths with gas turbines and radiant heaters.

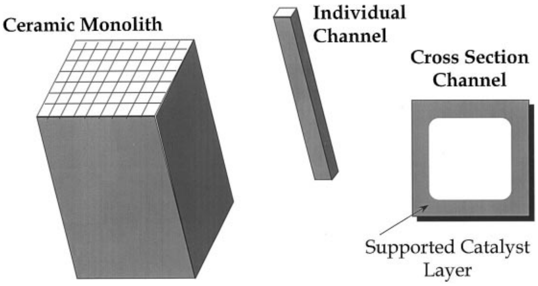

Fig. 6. Monolith, individual monolith channel, and cross-section of channel with catalytically active porous layer.

To ignite a homogeneous gas-phase combustion metallic gauzes are very attractive. Platinum or palladium gauzes are being utilized in the selective oxidation of ammonia to nitric oxide and in the reaction of ammonia with methane to hydrogen cyanide according to Andrussow. Since metallic gauzes can be preheated electrically, the start-up proceeds smoothly. However, platinum and palladium gauzes used in the selective oxidation of ammonia disintegrate already at around 800°C; in technical installations the resulting precious metal dust is being captured by a platinum or palladium gauze installed underneath the gauze performing the catalytic oxidation. The temperature of metal gauzes igniting the homogeneous gas-phase combustion of methane may be higher than that of the gauzes used in the selective catalytic oxidation of ammonia. Consequently the stability of the present metal gauzes is not likely to be sufficient to be utilized effectively in the ignition of the homogeneous gas-phase combustion of methane. Nevertheless it may be worthwhile to develop metal gauzes that can be heated electrically and are stable to oxidizing conditions at temperatures of the order of 1000°C.

5. Commercial monoliths

The commercial production of monoliths has been strongly stimulated by the utilization in automobiles to

Table 2
Properties of ceramic and metallic monoliths

Ceramic monoliths				
Cell density per inch^2	200	300	400	600
Wall thickness (mm)	0.3	0.3	0.15	0.15
Channel size (mm)	1.5	1.14	1.14	0.9
Open area (%)	69	63	77	73
Surface area (m^2/m^3)	2200	2740	3088	3790
Metallic monoliths				
Cell density	18			600
Wall thickness (mm)	0.13			0.05
Open area (%)				89

abate air pollution by exhaust gases. Corning has been leading in the production of ceramic monoliths. Also metallic monoliths [15] are produced commercially, though ceramic monoliths have dominated the field thus far. Two different types of ceramic monoliths can be distinguished, viz., monoliths of a limited porosity, and monoliths of a porous solid that simultaneously acts as a catalytically active component. The latter monoliths are mainly the monoliths used in the selective catalytic reduction of nitrogen oxides in flue gas with ammonia. The catalyst is vanadium oxide supported on titania, and the monolithic blocks are produced from titania of a high surface area. Monoliths are also produced from alumina of a high surface area. The ceramic monoliths used in automotive applications are mainly produced from cordierite, a combination of oxides of a composition $2MgO{\cdot}2SiO_2{\cdot}5SiO_2$. Cordierite has a low coefficient of thermal expansion and is even more stable after firing due to oriented growth of crystallites. Also mullite is used for the production of monoliths, which has the composition $3Al_2O_3{\cdot}SiO_2$. The dimensions of cordierite monoliths are summarized in Table 2. The surface area of the walls of the monoliths per unit volume is significant, but much smaller than the surface area of a fixed bed of, e.g., alumina of 250 m^2/g, which amounts to 3.75×10^8 m^2/m^3 for a bulk density of 1.5 g/ml.

Metallic monoliths have to withstand oxidizing conditions. Alloys that are stable in an oxidizing environment at elevated temperatures are Fecralloy, an alloy containing aluminum (0.5–12%), chromium (20%), yttrium (1–3%), and iron, and kanthal, an alloy containing aluminum (5.5%), chromium (22%), cobalt (0.5%), and iron. The stability of these alloys is due to segregation of a dense protecting layer of alumina on the surface of the alloys. Due to the presence of alumina at the surface, however, welding of the alloys is hardly possible. An important difference between ceramic and metallic monoliths is the thermal conductance of metallic monolith being much larger.

The amount of solids per unit volume is fairly small with monoliths. Especially metallic monoliths are containing a very limited amount of metal per unit volume. As a result, the heat capacity of usual monoliths is very low, which leads to rapid heating and cooling. With automotive catalysts, where rapid heating is highly important, a low heat capacity is important. Another essential feature of ceramic monoliths is the resistance against thermal shocks.

6. Application of catalytically active components to the walls of monoliths

With ceramic monoliths of a low surface area and with metallic monoliths the active component is almost invariably present on the walls of the monolith supported on a finely divided support. It is therefore useful to distinguish a primary and a secondary support. The primary support is the monolith and the secondary support the material onto which the active component has been applied. The secondary support is generally alumina, which is thermally stabilized by addition of, e.g., lanthanum oxide or silica. The stabilizing agent impedes recrystallization of γ-alumina to α-alumina; recrystallization to α-alumina leads to sintering and consequently to a severe drop in surface area. To suppress effectively the reaction to α-alumina, the lanthanum oxide or the silica has to be distributed uniformly over the surface of the alumina. Fig. 7 shows the configuration of the primary and secondary support within a monolith. Usual procedures involve applying either the pure secondary support on the walls of the monolith and subsequently loading the secondary support with the active component or first loading the secondary support with the active component and subsequently bringing the loaded secondary support on the walls of the monolith. Often a precursor of the active component is applied, which is converted by a thermal treatment in the active species. The above two procedures are schematically represented in Fig. 8.

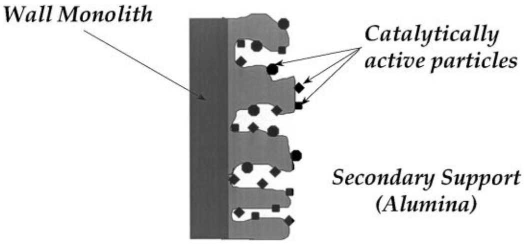

Fig. 7. Primary (monolith) and secondary (usual alumina) support.

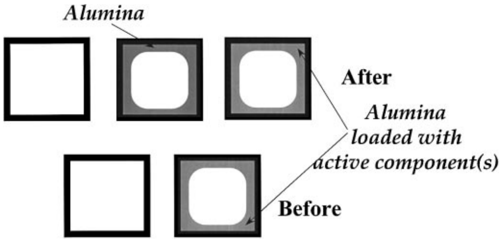

Fig. 8. Top: Initial application of bare secondary support onto walls of monolith followed by application of catalytically active precursor into porous layer of secondary support. Bottom: Application of secondary support previously loaded with active precursor onto walls of monolith.

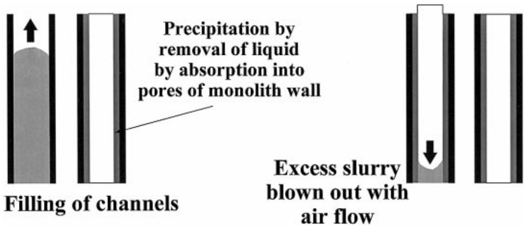

Fig. 9. Application of suspension of secondary support onto walls on monolith channels.

The preferred procedure to apply the secondary support before or after loading with the active component is dip-coating or wash-coating. As indicated in Fig. 9 the channels of the monolith are filled with a slurry of the secondary support. Pores present in the walls of the monolith will take up water from the elements of the slurry at the wall of the monolith. As a result a layer of the solid suspended in the slurry will be deposited on the walls of the monolith. The amount of solid deposited depends on the porosity of the walls of the monolith. Evacuation of the monolith prior to filling the channels with the slurry may raise the amount of solid deposited. Subsequently the remaining slurry is blown out of the monolith channels by an air flow as indicated in Fig. 9. The deposition of the solid on the wall of the monolith depends also on the electrostatic charge of the suspended solid particles and on the thixotropy of the suspension [16].

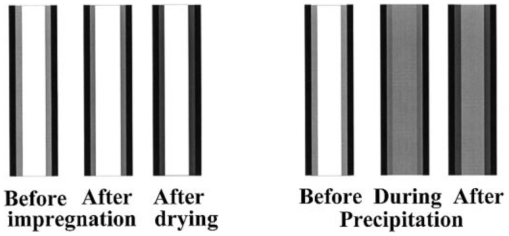

Fig. 10. Initially bare secondary support applied onto walls of monolith channels. Left-hand side: Application of active precursor on secondary support by impregnation. Right-hand side: Application of active precursor by deposition–precipitation.

The walls of metallic monoliths are more difficult to coat with a strongly adhering layer of a secondary support. Usually alumina whiskers are grown out of the surface of the aluminum alloys by keeping the monoliths at elevated temperatures in air. The alumina whiskers, which are strongly attached to the surface of the walls of the monoliths, are bonding the particles of the secondary support strongly.

When a bare secondary support has been deposited on the walls of a monolith, a precursor of the active component must be applied subsequently. Fig. 10 shows two procedures. Most obvious is impregnation of the layer of the secondary support with a solution of a precursor of the active component and drying. Especially impregnation with organic complexes of the active component, such as, citrates or EDTA complexes, leads to excellent results. The impregnation procedure is indicated on the left-hand side of Fig. 10. On the right-hand side, the procedure using deposition–precipitation is shown. The pores are filled with a solution of the precursor from which subsequently a compound is precipitated from a homogeneous solution. The precipitation is performed under conditions where the precipitate nucleates preferably on the surface of the secondary support.

Extensive research carried out to improve monolith reactors for automotive applications has provided procedures that result in coatings of ceramic monolith channels with precious metals that exhibit a good performance [16,17]. The application of coatings of non-precious metals, which are used at higher loadings, has been investigated much less.

7. Utilization of monoliths in gas turbines

Fig. 11 shows the temperature levels in a conventional gas turbine. It can be seen that the combustion leads to a gas flow of a temperature of 1500–2000°C. Hence the temperature at the inlet of the turbine cannot be higher than 1100–1300°C to avoid damage of the turbine wheel. To decrease the temperature fresh air is bypassed, as indicated in Fig. 11, to the inlet of the turbine. When the fuel content is decreased to lower the temperature behind the combustion chamber from 1100 to 1300°C, the combustion is not stable. At temperature levels of 1500–2000°C, however, nitrogen oxides are formed.

To abate air pollution by emission of exhaust gases of gas turbines two procedures have been proposed that do not use catalytic combustion. The first procedure involves ignition of a rich mixture, a quick quench with air, and a subsequent lean burn. With the initial rich mixture no nitrogen oxides are formed, while with the final lean burn the temperature remains thus low that no nitrogen oxides result. The problem with this procedure is the transition from the rich to the lean burn. The other procedure uses a lean premix burner, where the temperature also remains too low to lead to nitrogen oxides. With lean premix burners the stability of the combustion process is not sufficient, which calls for utilization of a diffusion burner. With catalytic ignition or catathermal combustion the homogeneous gas-phase reaction is initiated by a catalytic reaction. Fig. 12 shows the temperature levels with a catalytic combustor. It can be seen that the temperature now rises only to a level of 1100–1300°C, without passing through a maximum of 1500–2000°C.

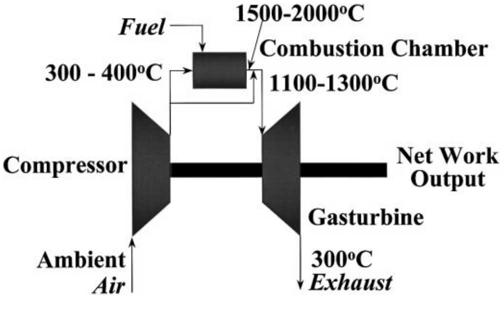

Fig. 11. Temperature levels with conventional gas turbine.

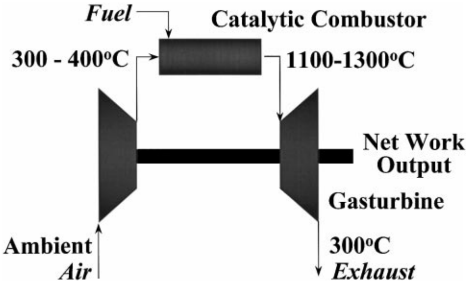

Fig. 12. Temperature levels with gas turbine with catalytic combustion.

Since a low pressure drop is a prerequisite with gas turbines, a monolithic reactor is obvious. Stable metal gauzes that can ignite the homogeneous gas-phase reaction have thus far not been produced on a large scale. It is obvious that the channels of monoliths completely prevent axial mixing. To avoid high temperatures in some channels the fuel–air mixture has therefore to be homogenized completely before entering the monolith structure. Since bad mixing leads to a randomly varying distribution of volumes of a high fuel concentration throughout the monolith structure, all channels will be consecutively subjected to elevated temperatures, which results in a complete deactivation of the catalyst. An efficient static mixer in front of the monolith is very useful to achieve a uniform composition of the gas flow entering the monolith.

The small diameter of monolith channels does not promote axial mixing within a channel. To achieve turbulent flow, which leads to efficient axial mixing, Reynolds number, which is proportional to the diameter of the channels, should be larger than about 2000. Only at very high linear velocities Reynolds numbers above 2000 are obtained with the narrow channels characteristic of monoliths. With gas turbines, however, very high linear velocities are used, which leads to turbulent flow also in the narrow channels of monoliths. The transport of the gas molecules to the walls of the monolith, where the catalyst is located, will proceed therefore sufficiently fast with monoliths used with gas turbines.

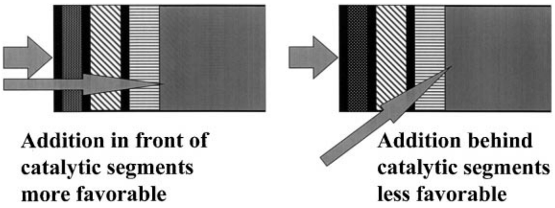

Fig. 13. Modes of introduction of fresh fuel into homogeneous combustion zone.

To maintain the temperature in the monolith at lower levels to avoid catalyst deactivation, it is attractive to limit the content of fuel gas of the flow fed to the monolith and to add the fuel required to establish the final temperature to the homogeneous gas-phase combustion zone. Fig. 13 shows two alternatives for the addition of fresh fuel gas. Since it is difficult to achieve a completely homogeneous mixture within the hot combustion zone, mixing is performed preferably in front of the monolith. Fresh gas is passed through the monolith to the homogeneous gas-phase combustion zone. According to a procedure mentioned by Catalytica, a monolith is used that has a number of channels the wall of which is bare. Since no catalyst is present in the channels, the fuel gas passes without reaction through the channels. To avoid the establishment of locally very elevated temperatures in the homogeneous gas-phase combustion zone, the fresh fuel must be mixed very efficiently into the gas flow. In Japan the arrangement of channels within the monolith has been optimized. In Fig. 14 the different arrangements studied are represented. The configuration at the right-hand side of the figure appeared to be the optimum.

The temperature required to ignite the homogeneous gas-phase reaction is about 800°C. It is highly important to assess the catalyst temperature that corresponds to a temperature of the gas flow of about 800°C. When the mass transfer proceeds more rapidly than the heat transfer does, the temperature of the catalyst can rise above the level of the adiabatic temperature rise (Fig. 15). The Lewis number indicates the ratio of heat transfer to mass transfer. With hydrogen Lewis numbers smaller than unity can arise readily; methane–air mixture, however, can also exhibit Lewis numbers smaller than unity at high temperatures. Consequently it can be expected that the catalyst temperature is 100–150°C above the temperature of the gas flow. Experimentally the difference in temperature between gas flow and catalyst has been confirmed.

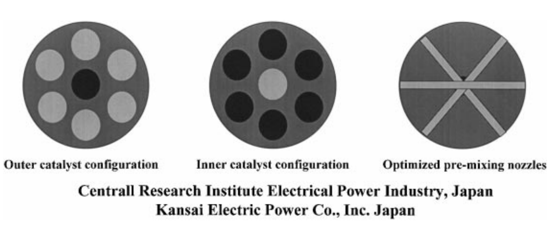

Fig. 14. Different configurations to introduce fresh fuel into homogeneous combustion zone.

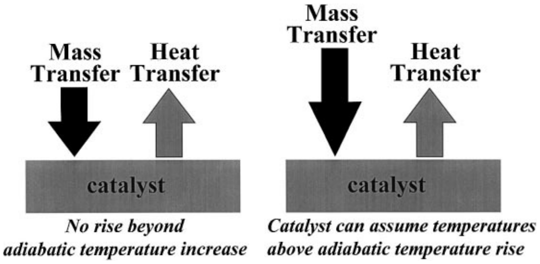

Fig. 15. Mass and heat transfer to surface catalyzing combustion reaction.

The most active catalyst in the combustion of methane is palladium oxide. To achieve a low light-off temperature palladium oxide is therefore generally used in catalytic combustion devices. Metallic palladium is considerably less active than palladium oxide. Since at temperatures above about 850°C palladium oxide decomposes to metallic palladium and molecular oxygen, temperatures above 850°C are critical. The activity of a palladium oxide catalyst steeply drops at higher temperatures due to the transition to metallic palladium. More serious is, however, the fact that the interaction between palladium oxide and an oxidic secondary support is much stronger than that between metallic palladium and an oxidic support. As a result decomposition to metallic palladium leads also to severe sintering of the supported palladium particles. To ensure the onset of the homogeneous gas-phase combustion a temperature of the gas flow of about 850°C is required, which corresponds to a catalyst temperature of about 1000°C. Since a palladium (oxide) catalyst is not stable at temperatures above about 850°C, another oxidic catalytically active component is required. Using radioactive tracers or

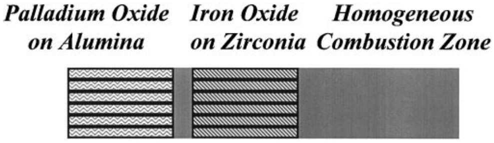

Fig. 16. Graded catalyst configuration; the first catalyst is an alumina-supported palladium oxide catalyst and the second catalyst zirconia-supported iron oxide.

Rutherford back scattering, the volatility of a number of candidate metal oxides has been established. Whereas copper(II) oxide and nickel oxide proved to be fairly volatile in the presence of steam, the volatility of iron oxide was established to be very low. A highly suitable secondary support for iron oxide was found to be zirconia. Accordingly a graded monolithic reactor appears to be most appropriate, as indicated in Fig. 16. Behind an effective static mixer an alumina-supported palladium oxide catalyst applied within a monolith is installed and subsequently a monolith containing zirconia-supported iron oxide catalyst.

Within a joint European Union research project Van Yperen (Degussa, Germany) applied palladium oxide catalyst on the walls of the channels of ceramic monoliths. To assess the kinetics of the combustion of methane the coated monolith was ground to bodies of about 0.5 mm which were installed in a small laboratory reactor at Utrecht University. The kinetics of the oxidation of methane within the resulting catalyst bed have been carefully measured. Actual measurements on the monoliths at elevated pressures were performed within the laboratory of GasUnie in Groningen. Using the experimentally determined kinetics Kolackowski and Awdry (Bath University) calculated the performance of a monolithic reactor at the elevated pressures relevant for gas turbines. The experimental results could be nicely reproduced by the calculations provided special attention was paid to entrance effects with the monoliths.

Compression of the gas flow will readily lead to an inlet temperature of about 350°C at the design load of the gas turbine. At low loads of the gas turbine, however, it is difficult to achieve the temperature required to light-off the catalytic reaction. A pre-burner is therefore utilized to run the gas turbine at low loads. A significant amount of nitrogen oxides is, however, produced by the pre-burner. A suitable metallic monolith can obviate the use of a pre-burner. With a sufficient thermal conductance a sufficient amount of thermal energy can be transported to the front end of the monolith to maintain the temperature at the light-off level of the catalyst. It may be considered to use a metallic monolith having walls of a sufficient thickness to provide the required thermal conductance.

Whereas the catalytic combustion of carbon monoxide proceeds much more rapidly than that of methane, the oxidation of carbon monoxide in the homogeneous gas-phase reaction is relatively slow. To completely oxidize the carbon monoxide intermediately formed during the oxidation of, e.g., methane, a catalyst may be helpful. The problem is to contact the carbon monoxide molecules with the catalytically active surface without a substantial pressure drop.

Performing the oxidation completely catalytically calls for monoliths that can withstand temperatures of 1100–1500°C. Within this temperature range a thermostable porous layer on the walls of the monoliths is not useful; the catalytic reaction proceeds so rapidly at these temperatures that the penetration into the pores is much slower. A non-porous catalyst structure is therefore sufficient. The homogeneous gas-phase reaction may be ignited within the channels of the monolith. When the homogeneous reaction releases an amount of thermal energy within a short length of the channel so large that the temperature of the monolith increases too much, the homogeneous gas-phase reaction should be suppressed by applying species effectively quenching free radicals on the walls of the monolith.

8. Monoliths used with radiant heaters

With the radiant heater a combustion reaction rapidly raises the temperature of a gas flow after which the gas flow is directed against a radiating body. To make available a high fraction of the thermal energy as radiation recirculation of the gas flow is necessary. For the combustion within a recirculating gas flow a monolithic reactor is appropriate. Whereas with gas turbines the linear flow rate of the gas is so high that back-flash of the homogeneous gas-phase reaction will not proceed., the gas flow rate is appreciably lower with radiant heaters. Consequently back-

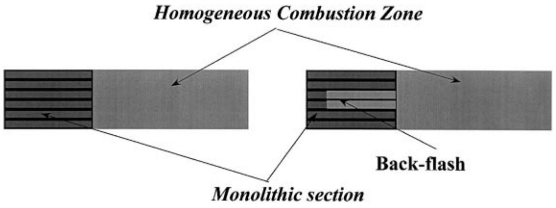

Fig. 17. Back-flash into monolith channels.

flash of the homogeneous gas-phase reaction can proceed as indicated in Fig. 17.

The oscillations of the catalytic combustion often observed with monoliths can be due to the formation of hydrogen by reaction of methane with steam produced by the combustion. At temperatures higher than about 800°C hydrogen can be produced in the homogeneous gas-phase reaction of methane and water

$$CH_4 + H_2O \rightarrow CO + 3H_2.$$

Back-flash with hydrogen can proceed more readily than with other combustible gases. When the homogeneous gas-phase reaction has penetrated towards the entrance of the monolith, the reaction is extinguished due to a concentration of hydrogen that is too small. Since the amount of water is small near the entrance of the monolith, not much hydrogen can be generated. As a result the catalytic reaction starts to dominate again, and the temperature at the exit of the monolith drops. When the homogeneous gas-phase reaction is re-ignited at the exit of the monolith, back-flash can proceed again. Since the catalyst sinters at the elevated temperatures established during the homogeneous gas-phase reaction within the channel of the monolith, the rate of the catalytic reaction drops and, consequently, the frequency of the oscillations. A flame arrestor can be very useful in suppressing the above oscillations.

9. Conclusions

The low pressure drop causes monoliths the structure of choice for catalytic combustions calling for a high final temperature. A substantial amount of industrial know-how is available for the production of monolith and for application of catalytically active components on the walls of the monoliths. However, development of monolithic combustion reactors by trial and error can be an extremely tedious and expensive process. Mathematically modeling of the catalytic reactor and the subsequent homogeneous gas-phase combustion can predict the performance of modifications of the installation much more rapidly than actual experiments. The extent of pre-mixing of the fuel gas has to be considered in the model as well as the entrance effects of the monoliths. Also the length of the monoliths required for the desired combustion or for ignition of a homogeneous gas-phase combustion has preferably to be calculated. The ability to predict the extent of the reaction of steam and hydrocarbons of the fuel to hydrogen and carbon monoxide would be very helpful to appreciate the possibility of back-flash of homogeneous gas-phase reaction and the occurrence of oscillations.

Besides mechanical strength metallic monoliths are offering a higher thermal conductance, which can also be advantageous. However, the stability against oxidation of metals and alloys has to be considered as well as the ability to produce strong monoliths from stable alloys. The possibilities of metal gauzes have not much been investigated, mainly due to lack of sufficiently stable alloys. Nevertheless metal gauzes are used in other industrial processes successfully, which may suggest research on the development of stable alloys and on the use of gauzes in ignition of homogeneous gas-phase reactions.

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