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Materials selection and design of high temperature catalytic combustion units

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Abstract

The range of operating conditions of catalytic combustors focuses attention on low temperature reactivity and high temperature stability of materials. Under lean fuel:air mixtures, catalysts operate at low temperatures and improved reactivity is required. Metal–support interactions improve reactivity as demonstrated with precious metal–ceria systems. However the reasons for enhanced reactivity and the means of optimising the catalysts are still not clear. The need for high temperature stability has led to detailed studies of washcoats, with the mechanism of sintering and the means of prevention now being understood. The demands of still higher temperature operation re-opens the question of materials selection and of combustor design, with two bed systems appearing to offer several advantages. Reassessment of materials in the light of revised design parameters is required.

Keywords: Combustion; Materials selection and design

1. Introduction

Although the use of catalytic combustors is now common [1], their operation is not without disadvantages. The combustors can be used with a wide range of fuels and fuel:air ratios, but can easily overheat if the operating conditions are not controlled. Materials sintering can be expected at temperatures in excess of (0.3–0.5) × melting point [2] and the direct combination of nitrogen and oxygen to form nitrogen oxides is significant above ca. 1650°C. As a result, temperature control is particularly important.

Gas throughput can also be high (up to 35 m s^{-1} in a turbine) which results in performance being affected by chemical kinetics and by mass and heat transfer. Pressure drop considerations also affect the design [3].

The processes involved in catalytic combustion are well established [3]. As temperature is increased, reaction is initiated at a level that depends on the reactivity of the hydrocarbon and the catalyst. The reaction is controlled by the chemical kinetics to the point where heat generated by the oxidation is sufficient that mass transfer to the catalyst surface becomes rate controlling. The temperature of the system increases dramatically and homogeneous oxidation may be initiated in the gas phase near to the catalyst [3]. Eventually the supply of fuel or of oxygen is exhausted and the catalyst temperature stabilises. Any further change in the fuel or oxygen supply leads to stabilisation at a new temperature.

Four important parameters are immediately obvious. It is essential that catalytic combustion be initiated at and continues at as low a tempera-

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ture as possible, particularly where the fuel:air ratio is lean and the catalyst is relatively cold. Reactions at low temperatures are controlled by chemical factors and catalyst reactivity must be maximised to improve performance.

At higher temperatures, mass and heat transfer control reaction and the texture of the catalyst becomes important. The temperature of the catalyst during the approach to and at steady state may be very high, and thermal stability of the systems is an essential design parameter.

Finally, any changes in temperature resulting from changes in operating conditions result in thermal stress. Temperature cycling or on-off operation can cause catalyst failure.

Mathematical modelling is an important tool in design and is considered separately [4]. The present article is focused on the design and choice of materials for catalytic combustion units, with particular emphasis on enhanced catalytic activity at low temperatures and on improved thermal stability at higher temperatures. Although inter-connected, the two areas of concern will be considered separately.

1.1. Low temperature catalytic activity

A catalytic converter needs to perform over a range of fuel:air ratios, including very lean mixtures. Under such conditions, operating temperatures are low (ca. 150–200°C) and enhanced catalytic activity is desired.

It is generally accepted that the ease of oxidation of a hydrocarbon over a catalyst is related to the metal–oxygen bond strength [5]. "Volcano" plots relating activity to the metal–oxygen bond strength [6] show clearly that the precious metals are among the most active catalysts for total oxidation. Thus it is not surprising that precious metals are widely used in catalytic combustors [1,3] and in car exhaust catalysts, where oxidation is a major desired reaction.

The problem is then to enhance the low temperature catalytic activity of the precious metals. It may be possible to select a metal which is known to be a particularly active catalyst for a given fuel [7] but such solutions are of limited applicability. What is needed is a more general approach to the problem.

It is now recognised that metal–support interactions may be the best way to improve catalyst activity. Perhaps the best studied system has been the precious metals–ceria systems used in car exhaust catalysts.

Precious metals are distributed in a washcoat which contains various materials designed to improve thermal stability and to assist in odour control. The washcoat also contains materials added to improve reactivity. One such additive is ceria. Originally added as an oxygen storage component [8], it was soon realised that the capacity of the oxide was too low for a major contribution. Subsequent investigation showed that ceria enhanced catalytic oxidation [7,9] as well as catalytic steam reforming and the water gas shift reaction [10].

Studies of the role of ceria have been many and varied [8–12]. One seminal paper on the role of the oxide originated from Harrison et al. [7] who proposed that the enhanced activity was due to interactions across the precious metal–oxide interface. Carbon monoxide or hydrocarbons were suggested to adsorb on precious metals and to extract oxygen from ceria en route to total oxidation. The ceria was then suggested to be reoxidised, for example by extracting oxygen from nitrogen oxides.

This paper has generated much experimental work [8–12]. The major problem with the concept has been found to be the difficulty of reducing ceria [13,14]. Reduction was found to be somewhat easier when there were considerable crystal imperfections in the ceria but, even then, only ca 15% of ceria could be reduced [14], an observation that may account for the preferred use of such precursors in the preparation of exhaust catalysts.

The presence of precious metals was found to enhance the reduction of ceria, with the reaction occurring some 150°C lower than over the non-promoted material [10]. Metal–ceria interactions, at least in this respect, have an important effect on reduction reactions occurring in the catalyst.

Once reduced, the precious metal–ceria couple proved to be a very efficient reducing agent. Reoxidation with air was too fast to measure. Reduction of carbon monoxide led to the formation of carbon on the surface [10,13]. Oxygen could be extracted by the reduced ceria from water and nitric oxide, leading to the production of hydrogen and nitrogen respectively[10,13]. The overall redox mechanism this would appear to be in accord with the suggestions of Harrison et al. [7].

One has to question, however, the relevance of the proposed mechanism in the light of the light of the fact that only ca. 15% of ceria could be reduced. In this respect, the addition of zirconia to catalysts seems to be very beneficial [15]. Ceria–zirconia interactions are reported to lead to much more efficient redox cycles, although publications to this effect are not immediately obvious. Monoclinic zirconia appears to be preferred, and recent papers have focused on the preparation of such material [16]. Given the ease of addition and removal of oxygen from zirconia, the plausibility of reactions involving precious metal support redox couples improves.

Given that such metal support interactions are important, the preparation of the catalysts to maximise intercomponent contact must be also important [17]. The preparation of car exhaust catalysts has been and continues to be a matter of much commercial importance, involving such factors as layering of washcoats, controlled precipitation conditions etc. Little information is reported in the literature, for reasons which are fairly obvious. Some systematic study of the effect of washcoat preparation on metal support interaction and catalytic activity would be of considerable interest.

One further proviso is that any findings must be considered in the knowledge that the high temperatures associated with combustion may affect catalytic activities. In this connection it is now useful to focus attention on high temperature performance.

1.2. High temperature performance

The requirement of a catalytic combustor to withstand high temperatures without significant loss of activity is essential. The means of effecting this are many and various.

One very effective concept is to initiate oxidation using a catalyst with most of the reaction occurring in the gas phase downstream of the unit. The original concept of Pfefferle et al. [18] has now been developed into a working model of a hybrid combustor [1]. Catalytic reactions are controlled to maintain temperatures of ca. 800°C, and materials selection is more of a problem in the context of the subsequent gas phase oxidation.

Several factors need to be considered in the design of more conventional catalytic combustors. One approach is based on the fact that high catalytic activity is required to initiate oxidation. Once this is done, a second less active catalyst may be used which may withstand higher temperatures more successfully [1].

Finally, the choice of washcoat systems, although used widely, posess real difficulties for high temperature cyclic operations and in materials selection for these conditions.

The components of the catalysts may be considered in turn.

1.3. The support

Because of the requirements of low pressure drop, most supports are cast in the form of a monolith. Two excellent reviews have considered the design and construction of the monoliths [1,19], and only the more relevant properties will be considered here.

Monolith supports are chosen for high mechanical strength and thermal stability, and it may be necessary to increase one property at the expense of another. Of the ceramic supports, cordierite is the most widely used material despite the fact that the maximum temperature of use is quite low (ca. 1400°C [19]). Mullite or zirconia (Table 1) are more suitable for higher temperatures, but the porosity necessary for good washcoat adhesion may be hard to achieve.

In the context of materials selection, thermal and mechanical stability, together with catalyst–washcoat adhesion, are perhaps the most signifi-

Table 1
Thermal characteristics of some possible materials for monolith construction

Material	Upper temp. limit (°C)	Linear coeff. of thermal expansion, k^{-1}
Alumina (Torvex)	1 500	8×10^{-6}
γ-alumina	1 100	
α-alumina	2 070	
Silica	1 100	
Zirconia	2 200	11.8×10^{-6}
Corderiete	1 400	1×10^{-6}
Fecralloy	1 350	ca. 15×10^{-6}
Mullite	1 350	2×10^{-6}
Aluminium titanate	1 800	2×10^{-6}
Silicon carbide	1 650	$4.7\text{–}5.3\times10^{-6}$
Silicon nitride	1 540	3.7×10^{-6}

cant parameters. The thermal characteristics of metallic monoliths limit operation to below about 1300–1400°C [19] and of ceramic monoliths to ca. 1200–2100°C. However, metallic monoliths have a much higher thermal conductivity than ceramics and can be fabricated with a smaller cross section. This allows a higher cell density and a much greater surface:volume ratio [19,20]. Heat generated by combustion is removed rapidly from the catalytic site.

Adhesion of the washcoat can be a problem with metallic monoliths, but alloys are carefully chosen to produce a coefficient of thermal expansion close to that of the washcoat. This can produce problems when chemical changes are induced (see below). Adhesion can be improved by oxidising the surface [21].

All in all, metallic monoliths are preferred for high throughput applications provided that the operating temperature can be controlled. If not, ceramic monoliths must be used.

Factors that control selection of the monolith have been discussed in Refs. [1] and [19]. The only reservation with the articles is perhaps that they fail to emphasise sufficiently the necessity of considering monolith and washcoat as a matched pair.

1.4. The washcoat

Conventional washcoat materials are used to distribute catalysts, to enhance catalytic activity (see above) or to improve thermal stability. More recently, attention has also been focused on inducing catalytic activity in the washcoat itself.

Alumina is by far the most common washcoat material, but suffers from a loss of surface area resulting from phase changes at about 1000–1200°C [2]. As a result, considerable attention has been focused on thermal stabilisation of the oxide.

One approach has been to focus on the structure of the alumina, using novel methods of preparation in the absence or presence of additives to induce a more stable structure. The hypothesis that sintering could be minimised by preparing needle like crystals of alumina in which crystal–crystal contact was minimised was tested by a novel preparation involving the intermediate production of aluminium sulphate [22]. Arai and co-workers [23–25] have argued that a layered aluminate structure, somewhat similar to β-alumina, minimised diffusion of aluminium ions. In both cases, however, small amounts of additives such as baria were needed to achieve thermal stability.

Very recent studies have thrown much light on the role of additives in inhibiting the sintering of alumina [26]. Sintering was examined in the presence of rare earth and alkaline earth ions. The results show clearly that sintering is affected by the ion size of the additive, with maximal sintering being observed with minimal ionic radius of the additive ion. Similar results have also been observed by Mizukami et al. [27].

The use of lanthana or baria as a surface area stabiliser is well established [7,28], and the effect had been suggested to be due either to formation of a surface coating [28], or to substitution of the additive at anion vacancies [26]. DRIFTS examination of aluminas containing additives before and after sintering showed no major change in the spectra of OH groups on the surface [26]. No evidence of OH groups associated with the additive was obtained and the La/Al ratio, as measured by XPS, was the same at the surface as in the bulk.

These results strongly suggest that substitution of additives in the alumina lattice hinders both bulk and surface diffusion and, as a result, stabilises the alumina against sintering. There are obvious advantages in obtaining an intimate mixture of the alumina and the additive, and sol-gel methods of preparation would seem to offer much potential [29]. Alumina containing catalysts have been made by this route [30] but few references to washcoat preparation have been found [29].

These results focus attention on stabilisation by inhibition of mass transfer, mainly by rare earth or alkaline earth oxide additives. Similar effects can be achieved by the use of other additives.

Interest in stabilisation by the addition of silica is growing [1,30]. Beguin et al. [30] argued that addition of silica would decrease the number of cation vacancies, thereby decreasing sintering. They used silicon tetraethyl to dope the surface of alumina to ca. 1–3%, and found that the resulting alumina maintained a surface area of over 50 m^2 g^{-1} after heating to 1220°C for 24 h in the presence of steam. Silica is, however, known to be volatile in steam to some extent [2], and better long term stability may result from applications of sol-gel preparation methods. Patent references to the use of silica stabilisation methods tend to support this approach [1].

The importance of crystal shape and of silica coating has been reemphasised by Horiuchi et al. [31,32]. Fibrous crystals of alumina were prepared from aluminium carbonate dihydroxide and coated with silica [31]. The amount of silica was fairly critical if the formation of mullite was to be avoided [32] with ca. 2–4% silica being preferred. Heating to over 1300°C allowed retention of surface areas in excess of 35 m^2 g^{-1}.

Future demands for still higher temperatures in catalytic combustion may well lead to the use of materials other than alumina. Mercera et al. [33] have studied the use of stabilised zirconia, albeit at temperatures too low to be of interest. Magnesia has been found to maintain high surface areas even after heating to 1500°C [34], although some caution is needed in view of the known tendency for hydrolysis at lower temperatures [35]. Ledoux et al. [36] added urania to silicon carbide to produce a material shown to be thermally stable at 1000°C.

There remains considerable need for further study of materials stable at temperatures in excess of 1000°C.

An interesting concept is the introduction of catalytic activity to the washcoat. Perovskites are best considered in the section on catalysts. Hexa-aluminates and spinels, in which thermal stability is a major property, can be conveniently considered as catalytically active supports.

Arai and co-workers [23–25] have studied hexa-aluminates ($MO{:}6Al_2O_3$) and substituted hexa-aluminates ($M(M_2)_x\ Al_{11-x}\ O_{19-y}$) extensively. M, (Ba, Sr, Ca) induced thermal stability to the structures, apparently by favouring a layered aluminate structure. M_2 (Cr, Mn, Fe, Co + Ni) was added as an oxidation catalyst with Mn found to be the most active ion. Lifetime tests have been reported for $Sr_{0.8}La_{0.2}MnAl_{11}O_{19-y}$ used at 1300°C for up to 6400 h [25]. The surface area was not high (the value reduced from ca. 18 m^2 g^{-1} to ca. 4 m^2 g^{-1}) but the oxidation activity remained constant. This lack of deactivation was attributed, at least in part, to the careful preparation of homogeneous materials.

One other interesting system is based on spinels [37,38]. These complex oxides are not normally thought of as active oxidation catalysts, and their activity is often orders of magnitude lower than the component oxides. Nonetheless, their high thermal stability may offer some hope for the future.

A major factor in washcoat design in the problem of continuing adhesion of the washcoat to the support. A monolith with large pores (5–15 μm) and porosity of 30–40% is required to give good adhesion [19]. However the exact choice of washcoat material is determined by the properties of the particular monolith. What is desired is that the washcoat adheres to the support at high temperatures and when the temperature is cycled.

Careful consideration is given to adhesion, for example by matching the coefficients of thermal expansion of the support and the washcoat (Table 1). In the case of alloy supports such as Fecralloy, such considerations may even outweigh thermal stability limitations [19]. However, additional problems may result from changes in composition as reaction proceeds. Thus, for example, catalytic combustion of fuels containing sulphur can result in the formation of various sulphates in the washcoat. Resulting differences in the volume of the solids and in thermal expansion can induce adhesion problems and spalling.

There are three possible approaches to this problem, only one of which has been explored in any depth in the open literature. Matching thermal coefficients of expansion of the support and the washcoat forms an important design characteristic for combustors [19]. However a second route may be to improve adhesion by chemical bonding across the support-washcoat interface. In this context, work reported on heterogenising homogeneous catalysts [39] is relevant. Chemical bonds between alloys or ceramics and washcoats involving silicon or phosphorus would seem to offer possible improvements in adhesion.

Finally, the possibility of washcoat design to make allowance for possible impurities seems feasible. Sulphur and/or nitrogen are the most likely contaminants of a fuel, unless the combustor is to be used for specific purposes. Selection of washcoat materials that are resistant to the formation of sulphates or nitrates and/or selection of materials where the coefficients of thermal expansion do not change greatly on formation of sulphates or nitrates would seem possible alternatives. With this in mind, surface impregnation by silica [30] or the selection of silicon carbide [25] or aluminium titanate [40] would seem to offer possibilities. No reports of the testing of such materials with contaminated fuels have been found.

The effect of exhaust gas components such as sulphur oxides on the inorganic chemistry of the washcoat and on catalytic performance has not been studied in depth. This is surprising, given the almost certain presence of S containing molecules in the fuel. It has been shown that aluminium and cerium sulphates may be formed when sulphur trioxide is passed over the corresponding oxides [41]. The reactions are favoured thermodynamically up to about 500°C: above this temperature, the sulphates begin to decompose to the oxides. Little is known, however, about other changes that can occur in and between washcoat components except that changes induced by sulphur oxides can have a marked effect on catalytic activity.

Other components of exhaust gases may also cause changes in the catalyst. Lead salts are on obvious example, but there are other components which may or may not influence catalyst structure and activity. Again, some detailed study of the inorganic chemistry of the systems would be valuable.

1.5. The catalyst

At high temperatures, it is necessary to balance catalytic activity against other desirable properties. Given that combustion may be initiated at lower temperatures (possibly by a precursor catalyst bed) then mass and heat transfer may be more important than catalytic activity. The only exception to this may result from the necessity to remove the last traces of fuel from the exhaust gases.

With this in mind, it is necessary to recognise design essentials (high throughput, high thermal stability, good mass and heat transfer) and to question other aspects of design. Thus, for example, is it essential to maintain high surface areas provided combustion can be initiated in a precursor bed?

These arguments re-focus attention on catalyst activity and thermal stability. Although the oxides are, in general, less active catalysts than precious metals [2,3], are there other advantages that balance this disadvantage? With some exceptions the answer to this question is, in general, negative.

The first problem arises with oxide stability. The familiar twin peak pattern of catalytic activity has been reported across the transition metal oxides [1,2,5], with cobalt and manganese oxides being most active. Given that sintering is expected to become significant at temperatures between 1/3 and 1/2 of the melting point [2], few such oxides can be expected to be more stable than precious metals.

Secondly, it is often necessary to achieve high throughput. Creating monoliths from catalytically active oxides, while avoiding problems of washcoat adhesion, at best leaves unaltered the problems of high throughput with thick walled ceramic monoliths. Using oxides as a washcoat removes none of these problems.

It must also be remembered that catalytic combustion produces water, and high temperature steam — in the absence of any other stability problems — is a very deleterious sintering atmosphere [2]. Complex oxides such as perovskites, although active catalysts [38], may well deactivate or decompose in such atmospheres. Some complex oxides do, however, maintain activity, even under extreme combustion conditions.

Finally, the chemical stability of oxides must be considered in terms of the high temperatures of combustion. McCarty and Wise [42] have demonstrated an inverse relation between catalytic activity and oxide stability, and this is not unexpected from the ''Volcano'' activity/metal oxide bond strength curves [2,5].

Despite these disadvantages, some mixed or complex oxides seem to offer possibilities as active combustion promoters. Hexa-aluminates substituted with manganese, discussed in the washcoat section above, are one possibility, but there are others.

Most active catalysts are based on mixed oxides. Prasad et al. [43] have tested a mixed $Cr_2O_3 \cdot Co_3O_4$ catalyst for propane combustion at temperatures of up to 1100°C and de Collougue et al. [44] extended the work to consider $LaCrO_3$ supported on $MgAl_2O_4$. The high temperatures of operation would seem to demand combinations of oxides which, in turn, require close attention to preparation methods.

2. Conclusions

This review of catalytic combustion poses some unanswered questions. The evidence is that catalytic combustors will become more common and that operation at higher temperatures will be desired. What, then, will be the requirements of such systems?

It seems certain that activity at low temperatures will be desired. Practically, precious metals are the most active catalysts, initiating reaction as low as 170–200°C. Is it possible to enhance activity still further by the use of washcoat additives? Or will it be necessary to induce reaction at very low temperatures by the use of, e.g. methanol [43], followed by fuel switching at temperatures in excess of 200°C.

Catalytic combustion also leads to high temperatures and problems with materials selection. Most of these problems arise from the perceived need to maintain high catalytic activity with high thermal stability. Are such design criteria necessary?

Selection of a two bed system in which the reaction is initiated with an active catalyst in one bed while most of the oxidation (and heat generation) is completed in the second seems more realistic. What properties are then desired in the second bed? Most materials are catalytically active at 1000°C. Why not investigate materials that have good stability at higher temperatures and which show catalytic activity-possibly only at such temperatures?

In such a system one has to ask whether the use of a washcoat is still desirable. Hexa-aluminates or perovskites could well be cheap enough to cast in the form of monoliths. Given that reaction is initiated in one bed containing high surface area/high activity catalyst, is it necessary to try to maintain high surface areas in the second bed?

Such considerations, in turn, introduce new arguments. How does the thermal shock properties of a one component monolith stand up to combustor performance? Would thermal transport through metallic monoliths be sufficient to negate the advantages of one component active oxide monoliths?

It seems convenient now to review again the properties desired in a catalytic combustor. What is needed is some comparisons of catalytic activities at high temperatures, using materials which can be prepared to a texture that optimises mass and heat transfer. It may well be that such materials are cheap/effective enough to be cast as monoliths, thereby avoiding the problems of monolith/washcoat systems.

Catalytic combustors have been under the shadow of the car exhaust catalyst for long enough. It seems time to rethink the sacred cows. It is good to see the beginnings of such re-appraisals [1,23–25].

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