

Materials for Catalytic Gas Combustion

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Abstract – Catalytic combustion, which permits to burn lean fuel/air mixtures is the key to environmentally preferable utilization of natural gas as an energy source and to removal of organic combustible gases from industrial effluents. The range of potential applications of catalytic combustion is large and can vary in temperatures of operation. Successful wide implementation of existing and of new catalytic combustion technologies will largely depend on the availability of suitable low cost catalytic materials. Since no single material can meet all demands, development of new catalysts needs to be orchestrated with the specific requirements of a given technology. The challenge is to combine existing knowledge and expertise in the area of combustion catalysts with innovations in their synthesis, improved formulations and applications in new specific composite forms. This paper outlines the current state of art and then focuses on perovskites for applications below 1,000 K. Examples of highly active formulations and of further enhancement of their activity through controlled synthesis and suitable support combinations are given. Criteria for the design of highly performing materials for high temperature catalytic combustion are also presented.

Key words : Catalytic Combustion, Combustion Catalysts, Combustion Technologies

INTRODUCTION

Natural gas as well as other hydrocarbon gases are and will continue for some time to be an economical source of energy mostly released during their combustion. However, since classical flame combustion of stoichiometric mixtures produces very high temperatures in which large amounts of noxious nitrogen oxides are formed, more and more effort is made to develop methods permitting to lower the operational temperatures. This can be achieved most efficiently by burning with the help of catalytic materials lean fuel mixtures. Indeed, in the presence of catalysts, i.e. during catalytic combustion, very wide range of operational temperatures may be achieved. These temperatures may be dictated by the power output requirements, but depend mainly on the fuel/air ratio and the mode of operation. Physical characteristics and the activity of the catalyst material required by a given system may also influence the operating temperature.

The beneficial effect on the rate of combustion of some materials has been known for nearly two centuries, and catalytic combustion has been exploited in a number of processes including heat generation, for decades [Houdry, 1960; Zernike, 1967; Pfefferle and Pfefferle, 1987]. Since the late sixties the increasing awareness about the pollution problems has intensified and the interest to widen the range of catalytic combustion applications has been growing steadily [Prasad et al., 1984; Trimm, 1984; Pfefferle and Pfefferle, 1987; Spivey, 1987]. Over the last twenty years much effort has been made to develop suitable catalytic combustion technologies even for high power generation systems which need to operate at rather high temperatures [Pfefferle, 1978; Arai and

Machida 1991; Zwinkels et al., 1993; Dalla Beta et al., 1993]. Today, catalytic combustion based gas turbines are becoming reality [Dalla Beta, 1997].

Present needs for the development of a wider range of new efficient heat and power generating technologies and their wide implementation are obvious. Not surprisingly the research and development in this area is very active. Ultimately, the success in a large acceptance of environmentally friendly gas combustion technologies will depend on the availability of suitable low cost catalytic materials.

The aim of this paper is to outline the current state of art and to propose some possibilities for future developments.

APPLICATIONS AND REQUIREMENTS

Depending on the area of application, the mode of operation and the temperature the demands on the overall performance (activity, stability, resistance to poisoning), physical properties, microstructural characteristics and shape, as well as the economy of the catalyst material may vary greatly. The operation characteristics may simply be dictated by the power output requirements, in the case of heat and power generation, or by gas through-puts in other processes. With respect to the activity and its durability, temperature to which the material is going to be exposed is the most important parameter to consider. In fact, temperature of operation also influences the resistance to poisoning. Thus, temperature seems to be the most convenient and practical means of classification. Table 1 outlines the scope of the catalytic combustion applications and corresponding material needs.

1. Low Temperature Applications

Low temperature catalytic processes are characterized by ultra low, often below detection limit, i.e. zero emissions of nitric

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Table 1. Catalytic combustion applications and corresponding catalyst requirements

Temperature range	Applications	Principal requirements for catalyst performance	Suitable catalyst material	Catalyst form
500-950 K	zero NO _x heat generators VOC incineration radiant pads gadgets	excellent activity, high SSA complete oxidation resistance to poisoning low cost	Pd and other supported noble metals supported oxides (Co ₃ O ₄) (nickel)-cobalt based perovskites	fluidizable particles pellets honeycombs fiber mats
850-1,200 K	heat generators radiant heaters incinerators	high activity, high SSA (resistance to poisoning) good thermal stability low cost	Pt/thermally stabilized supports, (supported) iron or manganese based perovskites	pellets monoliths porous ceramic plates
> 1,200 K	gas turbines burners	very good activity high thermal stability resistance to thermal shocks low cost	bulk single phase refractory materials doped with transition metals	monoliths: honeycombs foams

oxide, provided the fuel does not contain nitrogen compounds.

Low temperatures, typically below 950 K, are obtained only with very lean (with respect to combustibles) mixtures, when operating in a quasiadiabatic mode. Nevertheless, in the case of radiant heating systems, low temperatures may be maintained with higher concentrations of fuel. Due to low heat output from very lean mixtures, a special attention has to be given to the mode of operation to assure autothermicity. Because of the low fuel concentrations and low temperatures the catalysts need to have an excellent activity. On the other hand, owing to these low temperature limits, the demands on the thermal stability of the catalysts are relatively easy to meet, but the risk of poisoning is higher.

1-1. VOC Incineration

Catalytic incineration of a variety of combustible gases and vapors from industrial effluents has been practiced for decades [Houdry, 1961; Houston, 1975; Spivey, 1987], but with increasing environmental regulations the interest in its wider application is fast growing [Vigneron et al., 1994; Shelley, 1995; Windawi and Chu, 1996]. Essentially, most of these technologies operate adiabatically in fixed bed type reactors where ultra lean mixtures have to be processed. Such reactors often suffer from reaction front creep. To remedy these problems, alternative technologies employing a flow reversal have been developed [Houdry, 1960; Houston, 1975; Matros and McCombs, 1994]. Flowreversal fixed-bed reactor has been shown as particularly effective for catalytic incineration of several VOCs such as toluene, or acetone [Chaouki et al., 1995]. Due to the need to destroy by combustion a variety of organic compounds, many of them containing sulfur or chlorine, the greatest demand on the catalyst may, apart from high activity, be the resistance to poisoning. Indeed, development of catalysts for complete oxidation of chlorinated organic compounds represents a great challenge. For this type of applications both pellets and monoliths are suitable. Nevertheless, monoliths are more and more preferred, especially for high throughputs of treated effluents.

1-2. Zero NO_x Heat Generators

Although at present most effort seems to be devoted to the development of adiabatic high power systems such as gas turbines, there is a need for low power heat generators for indus-

trial, commercial, or even domestic use. For example, direct heat processing of food and of many polymer products requires atmospheres free of nitrogen oxides and of other pollutants namely carbon monoxide and unburned fuel. For such applications the upper temperature limits would be set between 780 and 980 K. Thus, when operated adiabatically, the combustor would have to burn considerably lean mixtures. Recently, two different technologies have been proposed and successfully tested in a laboratory pilot-type reactors for such applications. One uses fluidized bed reactor [Foka et al., 1994], the other exploits reverse-flow fixed-bed reactor [Chaouki et al., 1994]. It is clear, that while both technologies require catalysts of high activity capable to achieve full conversions of gas fuels to carbon dioxide, and having good resistance to potential poisoning by commonly used gas fuels odorants, the demands on their physical characteristics and shape are totally different. For the fluidized bed reactor small fluidizable particles resistant to attrition are required, whereas fixed-bed reactor with flow reversal can potentially accommodate both pellets and monoliths.

2. Intermediate Temperature Applications

In a number of countries large volume of natural gas is combusted for residential, commercial as well as industrial heating, contributing thereby to the pollution. Although efforts are made to improve the efficiency of various burners, global conversion to catalytic or thermo-catalytic systems would be the best solution. It is true that a variety of such systems for industrial use exists since a long time [Weiss, 1962; Zemike, 1967; Saint-Just and der Kinderen, 1996], but much remains to be done in the case of residential and commercial applications.

3. High Temperature Applications

Gas turbines for medium and high power generation and co-generation systems represent the largest volume of gas combustion technologies to be converted to catalytic operation. Gas turbine engines for transportation could be included in this area. To satisfy the power demand, the temperatures of operation can not be reduced below 1,300 K for lower size, and below 1,600 K for 200 MW generators. These temperatures, at which the homogeneous thermal combustion becomes important, impose very high demands on the catalytic material which ideally should be capable to ignite the reaction at temperatures of compressed gas mixtures,

typically between 570 and 950 K, but at the same time should withstand the extreme operational conditions, i.e. high temperatures and relatively corrosive atmospheres (humidity, carbon dioxide) under very high flow-rates. Early efforts to develop such a material proved unrealistic, no presently known material can satisfy such demands. However, new hybrid type concepts of the catalytic bed permitting to combine materials of different characteristics, from highly active to highly temperature resistant, have been successful, and allow further accelerated development [Dalla Beta et al., 1993; Zwinkels et al., 1993; Dalla Beta, 1997].

THE CATALYST

Among the variety of gaseous fuels or combustible organic vapors which are candidates for catalytic combustion, methane is the most difficult to activate and as such requires the most active catalysts. It may therefore be assumed that catalysts capable to ignite methane at reasonably low temperatures, will ignite other combustibles at even lower temperatures. Thus, catalysts suitable for methane should be suitable for other compounds, except for chlorinated hydrocarbons.

To permit the initiation of (methane) combustion at as low temperatures as possible, removing thereby the need for extensive preheating, the catalyst has to have very high activity, demonstrated by low light-off temperature. At the same time, depending on the design of the reactor system, it may be required that the catalyst withstands temperatures up to 1,700 K, although in some applications it may be possible to combine several materials to satisfy the overall performance requirements.

1. Catalysts for Low and Intermediate Temperatures

1-1. Noble Metals and Their Oxides

At low temperatures (<800 K) palladium has long been known to outperform in activity for methane combustion all available materials, including platinum, by an order of magnitude [Anderson et al., 1961; Lee and Trimm 1995]. Due to this high activity, it can be used at loading as low as 0.1 % when supported on high surface materials such as aluminas, and therefore in spite of being relatively expensive, it becomes affordable in a number of applications. Indeed several excellent commercial palladium based catalysts of different performance and forms are available. However, at temperatures between 800 and ~1,100 K the activity may dramatically drop, especially in atmospheres of low oxygen concentrations. This is due to the dissociation of highly active palladium oxide to metal [McCarty, 1995]. The activity of palladium oxide can to some degree be stabilized by ceria, but the mechanism is still not well understood [Nunan et al., 1992]. By itself, ceria is a good methane oxidation catalyst [Choudhary and Rane, 1991; Zamar et al., 1995]. This in part may be due to its excellent oxygen ion conductivity [Dell and Hooper, 1978]. The "promoting" effect is not necessarily limited to ceria, other oxides of variable oxidation states, and good oxygen ion mobility may be used successfully. Additional drawback of palladium may be the strong inhibition of its activity by combustion products (water and carbon dioxide) [Ribeiro et al., 1994]. Furthermore, at low temperatures, palladium oxide, similarly as other metal oxide catalysts is easily poisoned by sulfur oxides.

For intermediate temperatures (800 to 1,200 K) platinum,

which resists relatively well to sulfur oxides poisoning still remains the catalyst of choice [Trimm and Lam, 1980; Lee and Trimm, 1995]. Nevertheless, although similarly as in the case of palladium, loading below 1 wt% provides required activity, the high price of platinum seems prohibitive for much wider use.

Other noble metals such as rhodium, or ruthenium exhibit high catalytic activity for combustion, but in view of their high price (rhodium) or volatility (ruthenium) they could hardly compete with palladium or even platinum.

1-2. Transition Metal Oxides

In the effort to find economical replacements for expensive platinum, the catalytic activity in oxidation of hydrocarbons of various single or mixed transition metal oxides has been studied extensively [Anderson et al., 1961; Blazowski and Walsh 1975; Prasad et al., 1980; Golodets, 1983]. Number of transition metal oxides, in particular those with spinel structure, has been shown as highly active [Prasad et al., 1980; Golodets, 1983]. Certainly, several properly formulated spinels (such as CuCr_2O_4 , or Co_3O_4), when prepared with large surface area have a good potential for specific applications, but their temperature limit is relatively low.

1-3. Perovskites

Originally proposed and investigated for potential use as automotive catalysts [Libby, 1971], the highly active lanthanum transition metal based perovskites $\text{La}_{1-x}\text{Sr}_x\text{MO}_{3-\delta}$ (where M can be Co, Ni, Mn, Fe, Cr, or their combination) had failed to become commercialized in that area, mainly because of their susceptibility to poisoning by sulfur bearing compounds often present in too high concentrations in automotive fuels [Yao, 1975; Voorhoeve, 1977]. However, recently perovskites attract new attention as potential combustion catalysts for fuels free of, or containing low levels of sulfurous compounds [Arai et al., 1986; Seiyama, 1993]. By special preparation techniques [Tejuca et al., 1989; Kirchnerova and Klvana, 1999] these catalysts may be produced with relatively high surface area and thereby higher activity, making them particularly attractive for low temperature applications. Indeed, some perovskite compositions have shown the potential to compete successfully with platinum [Arai et al., 1986; Klvana et al., 1996]. One example is given in Table 2 and in Fig. 1, where the performance of some supported perovskites developed specifically for use in new technologies [Foka et al., 1994; Chaouki et al., 1994] is compared with that of commercial catalysts. It should be noted that the activity of these catalysts is not necessarily optimized, better performance could be achieved. Recent studies have shown that cobalt-nickel based perovskite is not sensitive to low levels of mercaptan, commonly used as natural gas odorant [Klvana et al., 1997a, b].

Very important catalytic characteristics of perovskites, not found in noble metals or in a number of oxides of different structure, is their capacity for deep oxidation, i.e. formation of CO_2 rather than CO, even in fuel rich reaction mixtures [Klvana et al., 1996; Rehspringer et al., 1991]. This has been correlated with the perovskite structure, and it is also likely influenced by high oxygen ion mobility in oxygen deficient perovskites [Dell and Hopper, 1978; Choudhary and Rane, 1991].

2. High Temperature Catalytic Materials

Although the new hybrid designs allow for combustion initi-

Table 2. Kinetic parameters (apparent activation energy and the rate constant at 823 K) for the first order reaction model for several combustion catalysts

Catalyst	E_{app} kJ/mol	k_{823} $\mu\text{mol}/(\text{g}\cdot\text{s}\cdot\text{bar})$
Pd(0.2 %)/alumina pellets (Procatalyse)	92	5800
Pt(0.2 %)-Sn/alumina pellets (Procatalyse)	117	120
LSNC ^a powder	92	300
LSNC(7.5 %)/alumino-silicate particles	87	29
LSNC(32.5 %)/Kaowool	91	117
LSNCF(8.6 %)/alumina pellets	111	24

^a: LSNC denotes $\text{La}_{0.66}\text{Sr}_{0.34}\text{Ni}_{0.3}\text{Co}_{0.7}\text{O}_3$ perovskite; LSNCF denotes $\text{La}_{0.66}\text{Sr}_{0.34}\text{Ni}_{0.29}\text{Co}_{0.69}\text{Fe}_{0.02}\text{O}_3$

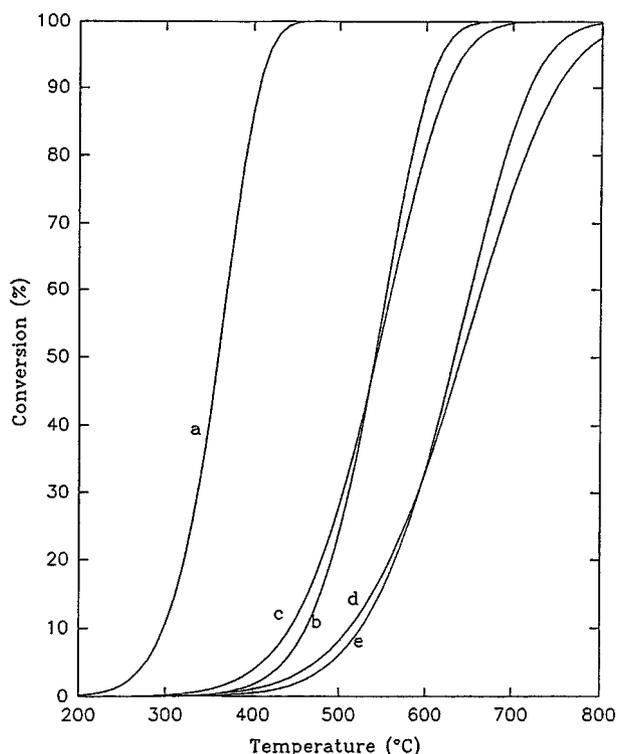


Fig. 1. Conversions as a function of temperature for several catalysts.

contact time 0.3 g s/ μmol ; a) 0.2 %Pd/alumina ; b) 0.2 % Pt, Sn/alumina ; c) LSNC (32.5 %) / Kaowool ; d) LSNC (7.5 %) /alumino-silicate fluidizable particles ; e) LSNCF (8.6 %) / alumina pellets

ation by highly active but less thermally stable catalysts, the need for catalytic materials capable to complete the combustion and withstand the extreme conditions remains. For the extreme conditions (>1,500 K, humid carbon dioxide containing atmospheres, high through-puts) the material has to have a high melting point, good thermochemical stability, very low volatility and preferably high thermal conductivity and emissivity to minimize local overheating. These stringent requirements on thermal stability of the material virtually rule out supported catalysts. No-

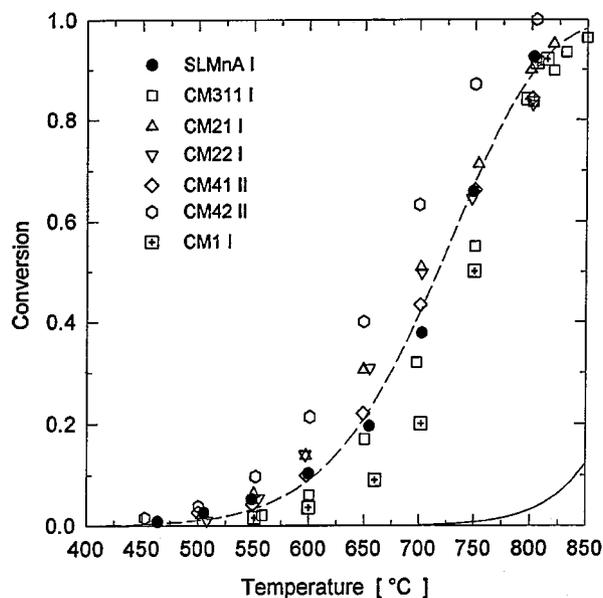


Fig. 2. Experimental methane conversions over new catalytic materials aged 7 h at 1,573 K. Full line represents conversions to carbon dioxide over pumice, broken line represents the conversions over $\text{Sr}_{0.8}\text{La}_{0.2}\text{MnAl}_{11}\text{O}_{19-\delta}$. Plug-flow reactor, 2 %methane/air, 400 mL/min, 1 g catalyst/10 mL pumice.

ble metals are too volatile and transition metal oxides are susceptible to react on the surface to form inactive phases. Solution to this problem can be found in doping highly stable refractory phases with transition metal oxides. Such materials have to be of rather low cost to permit their use as a bulk material for fabrication of suitable forms. An excellent example are the beta-alumina type phases doped with manganese, or with other transition metal oxides [Machida et al., 1987, 1990; Groppi et al., 1993]. Composition $\text{Sr}_{0.8}\text{La}_{0.2}\text{MnAl}_{11}\text{O}_{19-\delta}$ seems to be the best currently known high temperature catalyst. However, beta-alumina type ceramics exhibit very low resistance to thermal shocks. Development of alternative materials is therefore needed. These should be composed of nonvolatile oxides such as La_2O_3 , Al_2O_3 , CaO , CeO_2 , ZrO_2 , SrO . Barium oxide is too volatile for use at temperatures above 1,500 K. Of course the catalytically active dopants should also be selected from the least volatile transition metal oxides. Here, for example, chromium or copper oxides are not suitable.

High catalytic activity could potentially be found in other refractory phases doped at a sufficient level with the least volatile transition metal oxides. We have tested several new compositions of this type with very good results [Kirchnerova et al., 1998]. Table 3 gives some examples. All samples in Table 3 were prepared by a similar method based on freeze-drying reactive suspension consisting of carefully selected reactive precursor components. To permit a better comparison of the performance of the new materials with the activities of other catalysts, attempt was made to fit the conversion data by a first order model. In most cases very good fit was obtained. The resulting apparent kinetic parameters are given in Table 4, where k_{1000} is the rate constant for 1,000 K.

Table 3. Characteristics of new catalytic materials for high temperature combustion

Sample	Aging °C/h	SSA m ² /g	T ₁₀ °C	T ₅₀ °C	x ₇₀₀ %
SLMnA-I	1300/7	3.97	597	708	38
SLMnA-I 1300/14	1300/14	2.92	585	705	44
CM311-I	1300/7	1.37	610	745*	32
CM21-I	1300/7	2.04	575	700	51
CM22-I	1300/7	1.31	575	705	48
CM41-II	1072/4.5+1300/7	1.41	600	725	43
CM42-II	1072/4.5+1300/7	1.89	558	675	63
SLMnA-I 1450	1300/7+1450/6	0.74	700*	775**	23*
CM311I 1450	1300/7+1450/6	0.76	649	755**	10*
CM21-I 1450	1300/7+1450/6	0.70	700**	800***	11**
CM22-I 1450	1300+1450/6	0.59	650	802**	23*
CM41-II 1450	1300+1450/6	0.58	648	802*	22
CM42-II 1450	1300+1450/6	0.85	646	780	21
CM1-I	1300/7	2.75	670*	748*	19
CM1-I 1450	1300+1450/6	1.89	664	755*	20
SrZrO ₃	1300/7	5.0	665**	755***	8

For sample composition see Table 4, except for CM1-I which denotes Sr(ZrY)_{0.9}Mn_{0.1}O₃; T₁₀ and T₅₀ represent respectively temperatures at which 10 and 50 % methane conversion was observed; *, **, or *** behind indicate a presence of small, significant or large amount of carbon monoxide in the effluents; estimated on the basis of carbon balance; x₇₀₀ represents conversion to carbon dioxide at 700 °C (973 K).

Table 4. Apparent first order kinetic parameters for new catalytic materials aged 7 h at 1,573 K

I.D.	Sample composition	E _{app} kJ/mol	ln k ₀ , μmol/g·s·bar	ln k ₁₀₀₀ μmol/g · s · bar
SLMnA-I	Sr _{0.8} La _{0.2} MnAl ₁₁ O _{19.5}	106	18.1	5.3
CM311-I	SrTi _{0.8} Fe _{0.1} Mn _{0.1} O ₃	132	21.0	5.1
CM21-I	SrTi _{0.8} Fe _{0.2} O ₃	107	18.5	5.6
CM22-I	SrTi _{0.8} Fe _{0.2} O ₃	117	19.6	5.5
CM41-I	La _{0.85} Sr _{0.15} Al _{0.88} Fe _{0.12} O ₃	102	17.7	5.4
CM42-II	La _{0.85} Sr _{0.15} Al _{0.87} Fe _{0.09} Co _{0.04} O ₃	101	18.1	5.9

POTENTIAL DEVELOPMENTS

In view of the presented outline of the needs for catalytic combustion technologies and their current status following areas for future development may be identified :

- *High surface area supports for palladium with the capacity to stabilize the PdO to temperatures above 800 K.* Different forms of the catalyst (supported PdO) may be needed : agglomerating aerogel type particles for fluidized beds, or for use as washcoates, impregnated fiber blankets, impregnated monoliths such as honeycombs, foam-type, or sponge-type.

- *Alternative more economical ignition catalysts.* Again, emphasis has to be given to maximizing the intrinsic catalytic activity of a given material by very efficient preferably homogeneous dispersion and high surface area. This calls for a careful selection of support materials and innovative ways of impregnation techniques. Same types of catalyst form as cited above may find applications.

- *Efficient catalysts for complete catalytic oxidation of chlorinated organic compounds.* The main challenge in this area is to find a system showing durable activity. Most of the materials

currently known as good oxidation catalysts are easily poisoned by chlorides.

- *High surface area supported perovskites.* Presently, perovskites seem to show a high promise for industrial applications. When properly formulated and prepared, loadings of ~10 wt% may compete in performance with 0.2 wt%, in some cases up to 2 wt% Pt. Innovative methods of low temperature synthesis of perovskite powder as well as preparation of supported perovskites via in situ (on the support), techniques will be needed. High surface area powders could be deposited with the help of ceramic binders on the surface of porous supports.

- *High temperature catalytic materials.* First, the following question should be asked: for temperatures > 1,300 K is the large surface area really necessary ? Should not other characteristics, in particular, thermal conductivity, thermal expansion, and even intrinsic catalytic activity be given priority ? Volatility must not be forgotten. Ceramics with very low thermal expansion, some from the perovskite family, are known. When searching for materials with high thermal conductivity perhaps attention should again be given to some electronically conducting but thermally stable perovskites, which at the same time could satisfy the need of good intrinsic catalytic activity.

CONCLUDING REMARKS

Successful wide implementation of existing and the development of new catalytic gas combustion technologies will depend on the availability of reliable efficient low cost catalytic materials. The necessity for their development opens new opportunities and challenges for both scientific and industrial community working in the field of catalysis and of ceramic materials.

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