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Design criteria for high-temperature combustion catalysts

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In this paper design criteria used in the development of new highly active materials for high-temperature catalytic combustion of natural gas are presented with selected examples. It is the composition and structure of a given material which determine the activity. Specific surface area plays a secondary role.

Keywords: (high-temperature) catalytic combustion, mechanism of methane complete oxidation, transition metal substituted refractory perovskites

1. Introduction

The virtues of catalytic combustion have been known for more than a century [1], but only over the last three decades a systematic effort to develop suitable technologies and catalytic materials required for their operation has been made [2–7]. Dozens of materials ranging from supported noble metals [8] to single, bulk, supported, or mixed transition metal oxides have been tested [7,9–11]. In the early eighties considerable attention has also been given to lanthanum–strontium transition metal based perovskites [12,13] which by then have been known as excellent oxidation catalysts in a number of other oxygen involving reactions. Such perovskites have remained popular [14,15], but it became clear that their application is due to their easy sintering and/or limited thermal stability restricted to lower and medium temperatures of operation. Although some of them, in particular manganites and ironites, are fairly stable and exhibit a good activity still at about 1000 °C, the more active cobaltites lose their activity at around 800 °C. Assuming that large surface area is the key factor in enhancing the activity in catalytic combustion of a given material, more attention has later been given to materials exhibiting intrinsically high specific surface areas (SSA) such as transition metal substituted lanthanum–strontium hexaaluminates having β-alumina type structure [16,17]. Much attention has also been given to the preparation methods ensuring high SSA [18,19]. Among hexaaluminates $Sr_{0.8}La_{0.2}MnAl_{11}O_{19}$ has been found the most active, and so far has been considered as the most promising high-temperature combustion catalyst. Yet, although a very good catalyst, this material still does not seem to satisfy all requirements of thermal stability. For example when in the form of monoliths, it has a very low resistance to thermal shocks, caused primarily by a two-dimensional thermal expansion.

Using our expertise in the development of combustion catalysts [14,15,20], in the preparation of perovskites [21], and in the development of β-alumina type ceramics [22] we are currently developing in collaboration with Natural Gas Technology Center (Gaz Métropolitain and Gaz de France) new alternative materials. Our goal is to improve the resistance to thermal shocks by selecting materials exhibiting isosteric thermal expansion, and to develop simple low-cost preparation methods.

In this paper criteria used in the design and the preparation of new thermally stable catalytic materials are described and examples of catalytic performance in methane combustion of selected new materials are given. All materials were prepared by a simple method employing low-cost precursors and their effect on the formation of a new phase and its catalytic performance is also briefly discussed. To provide grounds for an objective evaluation of the effects on the catalytic performance of the composition and of the preparation method, the activity of two samples of $Sr_{0.8}La_{0.2}MnAl_{11}O_{19}$, one commercial (SLMnA-com) prepared via alkoxides, and one prepared in this laboratory (SLMnA-I) is discussed prior to that of the new materials.

2. Criteria for designing high-temperature combustion catalysts

To be suitable for a wide range of high-temperature catalytic combustion applications the material should be able to ignite lean methane/air mixtures at low temperatures (for practical reasons below 600 °C), but above all has to conserve high activity even after being exposed at temperatures above 1000 °C to high flow rates of combustion effluents.

The literature data and information [1–14,23 and references therein] permit to assume that the complete catalytic oxidation of methane and of other hydrocarbons proceeds in the following steps. The first step may be considered as the activation during which the first C–H bond is broken by the reaction with a surface bound oxygen species the nature of which is still not well known, i.e.,

$$H_3C\text{–}H + [O] \rightarrow [H_3C^{\cdot}] + [OH]$$

Next, the methyl radical $[H_3C^{\cdot}]$ must react on the surface with an electron acceptor and inevitably with an additional, rather labile, oxygen species favorably coordinated around the acceptor. This oxidation step leading to the formation of surface bound carbon dioxide and water proceeds most likely through some spillover type reaction. The surface bound carbon dioxide and water are finally desorbed. In the absence of an electron acceptor coordinated with active oxygen species the methyl radical desorbs and may undergo gas phase reactions leading to products other than carbon dioxide. In many cases desorption of carbon dioxide as well as of water are relatively slow processes, exerting thereby an inhibition effect on the overall rate of catalytic combustion [20].

In view of this mechanism, a highly active catalyst must have a sufficiently large number of two types of active sites: surface electron acceptors favoring fast electron exchange and highly mobile surface available oxygen. Palladium and other transition metal ions which may easily change their oxidation states in structures promoting fast reversible oxygen chemisorption apparently represent the highly desirable active sites. In addition, a good oxygen ion and electronic conductivity as well as a reasonable number of active sites are expected to enhance the activity. Nevertheless, to ensure high thermal stability, the satisfactory material must above all exhibit very low volatility and be reasonably resistant to sintering, i.e., have a very high melting point. Finally, to also allow a direct use in the form of monoliths, the material should have a relatively low, preferably tri-dimensional coefficient of thermal expansion.

Understandably, these criteria seem to restrict the choice to single-phase materials prepared from nonvolatile components by methods maximizing the formation of active sites at the surface, and minimizing their subsequent loss by exposure to combustion effluents at high temperatures. In fact, SLMnA β-alumina is a good example. Mixtures of different components, specifically supported transition metal oxides, are not suitable for high-temperature operations because of potential surface sintering or reactions with the support and loss of activity.

While it is known that activity of combustion catalysts increases with higher SSA, it has been shown that in the case of perovskites, SSA above 10 m^2/g have much less effect on the activity than expected [14,21]. Furthermore, since some loss of SSA during operation at high temperatures must be expected, it may not be necessary to maximize the initial SSA by complex costly preparation processes using expensive precursors.

3. Experimental

3.1. Catalyst preparation and characterization

The catalysts used in this study were prepared by simple, previously developed methods [21,22] using fine powders of low-cost reactive oxides such as lanthanum oxide, anatase, or yttria-stabilized zirconia, boehmite, and strontium carbonate (or nitrate) as precursors of the principal components. Transition metal (iron, manganese, cobalt) nitrates, or gamma iron oxide, were used as the precursors of the minor, catalytic activity bearing components. Care was taken to mix the components in strictly stoichiometric ratios. First, a fine highly homogeneous suspension of solids in the solution of salts was prepared by wet milling, typically for more than 2 h to promote maximum hydration. The proportion of solids/liquid was selected in a way to render the suspension sufficiently stable for further processing via freeze-drying. The suspension was frozen either by spraying, or by direct pouring in liquid nitrogen and dried under vacuum. The vacuum-dried precursor mixture was then calcined under controlled conditions, typically 10–16 h at 860 °C or higher depending on the composition, to form the desired phase. Finally, before evaluating the activity, the catalysts were aged by calcination in air at 1300 °C for 7 h, or longer, and additionally at 1450 °C for 6 h. Boehmite was used as the precursor of aluminum oxide also in the case of $Sr_{0.8}La_{0.2}MnAl_{11}O_{19}$ (SLMnA-I).

Formation of a desired phase was confirmed by X-ray diffractometry. Specific surface areas (SSA) of catalyst powders were determined by nitrogen adsorption (30% nitrogen/70% helium) on a Micromeritics Flowsorb 2300 apparatus using a single-point BET method.

3.2. Catalyst performance evaluation

The catalytic activity was evaluated in a horizontal plug-flow reactor consisting of an alumina ceramic tube with 1.3 cm internal diameter. The catalytic bed of 1 g catalyst powder, particle size <5 μm, mixed homogeneously with 10 ml pumice particles (350–500 μm), filled an annular space between the reactor tube and a thermocouple alumina sheath (0.64 cm diameter) passing in the center. This method of diluting the catalyst proved satisfactory to keep the bed quasi-isothermal [15,20]. The reaction mixture of 2% methane in air was flowing over the catalyst at 400 ml/min. The reactor was heated in steps of about 50 degrees. When a steady temperature was obtained the effluents were analyzed by gas chromatography, after removing water by a desiccant. For methane and carbon dioxide a Porapak Q column was used. When needed the presence of carbon monoxide was determined using a column packed with 5A molecular sieve.

4. Results and discussion

4.1. Catalyst design, preparation, and characteristics

To be thermally stable, any material for the high-temperature combustion has to be above all nonvolatile. Among the common oxides those of zirconium, titanium, aluminum, lanthanum, and calcium are the least volatile [24,25] and should be considered as the basic components of such materials. However, calcium has the tendency to produce phases with very low specific surface

Table 1
Compositions and some preparation conditions of catalytic materials studied.

Sample	Composition	Cation ratio[a] act/inact	Precursors	Initial calcination (°C/h)	SSA[b] (m^2/g)
SLMnA-I	$Sr_{0.8}La_{0.2}MnAl_{11}O_{19}$	1/12	$Sr(NO_3)_2$, La_2O_3, boehmite, Mn nitrate	1150/26	7.5
CM311-I	$SrTi_{0.8}Fe_{0.1}Mn_{0.1}O_3$	1/9	$SrCO_3$, anatase, γ-Fe_2O_3, Mn nitrate	980/16	3.2
CM21-I	$SrTi_{0.9}Fe_{0.1}O_3$	1/19	$SrCO_3$, anatase, γ-Fe_2O_3	980/16	3.6
CM22-I	$SrTi_{0.8}Fe_{0.2}O_3$	1/9	$SrCO_3$, anatase, $Fe(NO_3)_3 \cdot 9H_2O$	980/16	3.6
CM41-II	$La_{0.85}Sr_{0.15}Al_{0.88}Fe_{0.12}O_3$	1/15.7	La_2O_3, Sr, Al nitrates, γ-Fe_2O_3	620/9	18
CM42-II	$La_{0.85}Sr_{0.15}Al_{0.87}Fe_{0.09}Co_{0.04}O_3$	1/14.4	La_2O_3, boehmite, Sr, Fe, Co nitrates	1070/26	8.1
CM1-I	$SrZr_{0.83}Y_{0.07}Mn_{0.1}O_3$	1/19	$SrCO_3$, ZrO_2/(8 wt%)Y_2O_3, Mn nitrate	1000/16	3.8
	$SrZrO_3$		$Sr(NO_3)_2$, $Zr(SO_4)_2 \cdot 4H_2O$	860/10	12

[a] Ratio of active/inactive cations in the composition.
[b] SSA after calcination leading to β-alumina or perovskite phase formation.

areas. Therefore, strontium oxide had to be included in the formulations, in spite of its relatively high, with respect to other refractory oxides, volatility. From the catalytically active transition metal oxides, iron oxide is the least volatile and was therefore targeted as the most suitable, but manganese, cobalt, and nickel were also considered as dopants. Barium, copper, and chromic oxides are prohibitively volatile for use at temperatures above 1150 °C [24,25].

In view of the outlined criteria and mechanism of catalytic combustion, transition metal substituted refractory perovskites such as lanthanum aluminate, strontium zirconate, or strontium titanate seemed to be excellent candidates. The perovskite structure seems to promote deep oxidation [20], and its coefficient of thermal expansion is isosteric. It is worth mentioning that the use of pure (non-substituted) refractory perovskites, which by themselves exhibit very low activity for the complete oxidation, as potential supports for transition metal oxides has already been studied in several laboratories [26–28], without much success, however. Considering the potential surface sintering of the active phase as well as its possible reaction with the support this is not surprising.

With respect to the level of doping very little information is available. Nevertheless, based on percolation theory, 20 at% of the B site of the perovskite formula ABO_3 may be estimated as the upper limit. Actually, at 10% substitution the ratio of active/inactive cations is 1/19, increasing to 1/9 for 20% substitution. In $Sr_{0.8}La_{0.2}MnAl_{11}O_{19}$ the corresponding ratio is 1/12. A higher level of substitution is expected to lower the temperature of sintering and therefore the upper temperature at which a high catalyst activity can be maintained.

When preparing very active single-phase mixed oxide catalysts the main challenge is to form the required pure phase with extensively defective surface. To avoid loss of surface defects (activity) by local reactions and sintering during extensive exposure to high temperatures, homogeneity of the catalyst seems far more important than in the case of catalysts for applications at lower temperatures. Thus, the preparation should start with a sufficiently homogeneous mixture of precursors selected in a way to promote the formation of the new phase at temperatures below that of the anticipated operation of the catalyst. It is undoubtedly for this reason that the so far preferred preparation methods use aqueous solutions as precursors [18,19], or even alkoxides to maximize SSA [17]. While (in the case of β-aluminas) the alkoxide-based preparation method leads to excellent activities, its cost is relatively high and its ultimate advantage still remains to be confirmed by long-term tests. Even alkoxide-derived samples of β-alumina lose their initially high activity, albeit slowly.

The composition of selected new materials, precursors employed for their preparation, initial calcination conditions used to form the new phase and resulting SSA are presented in table 1. The indicated conditions needed to obtain a nearly pure perovskite (or β-alumina) phase were in most cases preceded by calcination at lower temperature. The overall thermal treatment may have some effect on the rate of SSA loss during aging, and consequently on the catalytic performance.

All precursor oxides were very fine powders, except boehmite, having SSA of the order of 10 m^2/g. SSA of boehmite was 110 m^2/g, whereas that of strontium carbonate was 5 m^2/g. It is believed that the wet milling of the precursor suspension increased the activity of the oxides to form a new single phase (β-alumina or perovskite) at relatively low temperatures. These depend on both the phase type formed and precursors. For example, formation of the β-alumina phase required calcination above 1100 °C for several hours. Although the SSA of the precursor mixture was 80 m^2/g after the precalcination at 860 °C, it dropped to 7.4 m^2/g after calcination 26 h at 1150 °C when a pure β-alumina phase was obtained, and to 4 m^2/g after subsequent aging 7 h at 1300 °C (table 2). In contrast to β-alumina, which is formed only at relatively high temperatures [22], formation of a perovskite phase takes place at significantly lower temperatures and depends strongly on precursors. For example, formation of strontium titanate required calcination at 980 °C for 12 h when using strontium carbonate as a source of strontium oxide, but with strontium nitrate replacing the carbonate perovskite was formed at 800 °C. The formation of lanthanum aluminate perovskite depends greatly on the precursor of aluminum oxide. When

Table 2
Characteristics of new catalytic materials for high-temperature combustion.

Sample[a]	Aging (°C/h)	SSA[b] (m^2/g)	T_{10}[c] (°C)	T_{50}[c] (°C)	X_{700}[d] (%)
SLMnA-com	1300/7	13.0	520	615	85
SLMnA-com	1300/14	10.6	520	625	82
SLMnA-I	1300/7	4.0	590	705	42
SLMnA-I	1300/14	2.9	595	707	40
CM311-I	1300/7	1.4	610	745*	32
CM21-I	1300/7	2.0	575	700	51
CM22-I	1300/7	1.3	575	705	48
CM41-II	1072/4.5 + 1300/7	1.4	600	725	43
CM42-II	1072/4.5 + 1300/7	1.9	558	675	63
SLMnA-com 1450	1300/7 + 1450/6	3.0	575	690	53
SLMnA-I 1450	1300/7 + 1450/6	0.7	700*	775**	23*
CM311I 1450	1300/7 + 1450/6	0.8	649	755**	10*
CM21-I 1450	1300/7 + 1450/6	0.7	700**	800***	11**
CM22-I 1450	1300/7 + 1450/6	0.6	650	802**	23*
CM41-II 1450	1300/7 + 1450/6	0.6	648	802*	22
CM42-II 1450	1300/7 + 1450/6	0.9	646	780	21
CM1-I	1300/7	2.8	670*	748*	19
CM1-I 1450	1300/7 + 1450/6	1.9	664	755*	20
$SrZrO_3$	1300/7	5.0	665**	755***	8***

[a] For sample composition see table 1.

[b] All SSA determined before activity evaluation.

[c] T_{10} and T_{50} represent, respectively, temperatures at which 10 and 50% methane conversion was observed; *, **, or *** indicate a presence of small, significant, or large amount of carbon monoxide in the effluents; estimated on the basis of carbon balance.

[d] X_{700} represents conversion to carbon dioxide at 700 °C (973 K).

boehmite was used, a temperature above 1000 °C had to be employed to achieve a full conversion to the perovskite phase, although its formation was observed starting at about 900 °C. When aluminum nitrate was used, formation of perovskite was complete below 700 °C.

Similar dependence on precursor was observed in the case of strontium zirconates. When using yttria-stabilized zirconia, a temperature above 1000 °C was needed to obtain pure perovskite. On the other hand, formation of $SrZrO_3$ prepared via the sol–gel technique using zirconium sulfate and strontium nitrate as precursors, was complete on calcination several hours at 800 °C and its SSA was about 20 m^2/g. Nevertheless, the SSA of the latter sample gradually decreased on further thermal treatment, similarly as already observed by others [26,29].

4.2. Catalytic performance of $Sr_{0.8}La_{0.2}MnAl_{11}O_{19}$ as a function of SSA

To provide a solid basis for evaluation of the catalytic performance of the new materials, the activity of two samples of $Sr_{0.8}La_{0.2}MnAl_{11}O_{19}$, one commercial, prepared via alkoxides (SLMnA-com), the other prepared by the above described method using low-cost precursors (SLMnA-I), were used for comparison. Each was in addition aged under similar conditions. On aging, the catalytic activity of both samples decreased, as shown in figure 1 and by selected activity data such as temperatures of 10 and 50% conversion to carbon dioxide and conversions at 700 °C given in table 2. This decrease seems to parallel the loss of SSA by aging prior to activity evaluation. The SSA of the as-received SLMnA-com sample was 21 m^2/g, whereas the initial SSA of SLMnA-I was only 7.5 m^2/g. These data clearly indicate that the specific activity of SLMnA-com is superior to that of SLMnA-I. It could therefore be concluded that, in spite of a reasonably good apparent activity exhibited by SLMnA-I, the new preparation method does not ensure high activity. However, a different picture is obtained when the activities expressed in terms of SSA, i.e., areal activities, are compared. To permit such a comparison the conversion data of figure 1 were fitted by an integrated simple first-order rate model which for a given contact time gives a very good fit, as shown in figure 2. The resulting

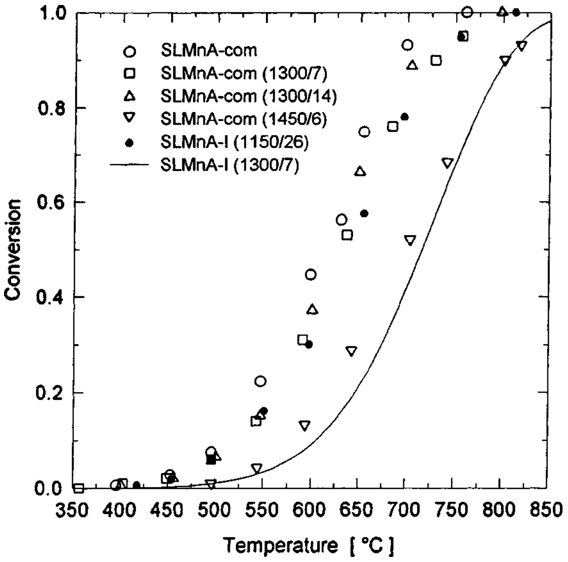

Figure 1. Experimental methane conversions over two samples of $Sr_{0.8}La_{0.2}MnAl_{11}O_{19}$, commercial (SLMnA-com) and one prepared by a simple method (SLMnA-I), both calcined under different conditions. Plug-flow reactor, 2% methane/air, 400 ml/min, 1 g catalyst/10 ml pumice.

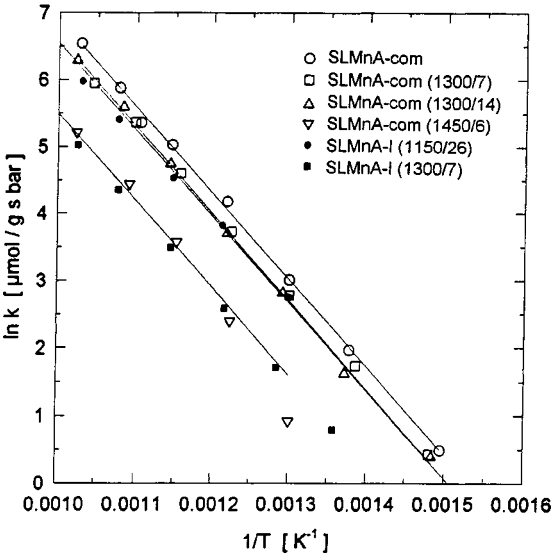

Figure 2. Arrhenius plot of an integrated first-order kinetic model for data of figure 1.

Table 3
Apparent first-order kinetic parameters for $Sr_{0.8}La_{0.2}MnAl_{11}O_{19}$ as a function of SSA.

Sample	SSA (m^2/g)	E_{app} (kJ/mol)	ln A (μmol/(g s bar))	k_{1000} (μmol/(g s bar))	k'_{1000} (μmol/(m^2 s bar))	k_{823} (μmol/(g s bar))	k'_{823} (μmol/(m^2 s bar))
SLMnA-com[a]	21	107	19.8	982	47	61	3
SLMnA-com	13	108	19.6	742	57	45	3
SLMnA-com	10.6	109	19.7	700	66	43	4
SLMnA-com	3.0	117	19.6	240	80	12	4
SLMnA-I[b]	7.4	99	18.2	540	73	42	6
SLMnA-I	4.0	101	17.8	284	71	21	5
SLMnA-I	2.9	100	17.5	230	79	17	6

[a] As received (original); on calcination in the laboratory under conditions similar to those of other materials the SSA gradually decreased.

[b] Single-phase SLMnA-I, obtained by calcination for 26 h at 1150 °C.

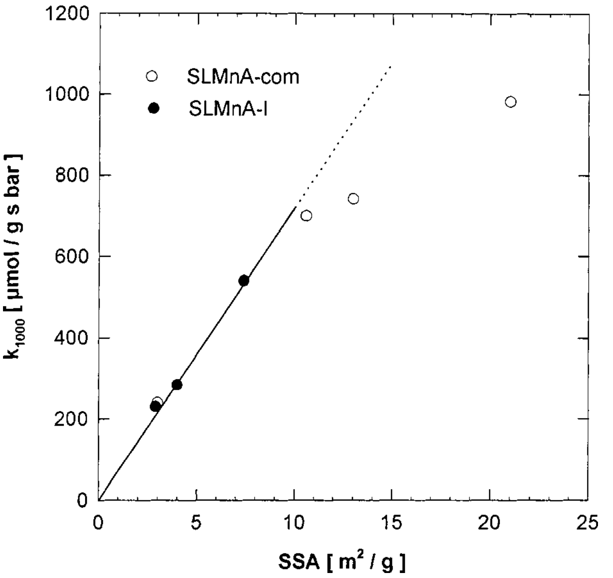

Figure 3. Apparent first-order kinetic constant k_{1000} for the catalytic combustion of methane over samples of SLMnA catalyst as a function of SSA, data from table 3.

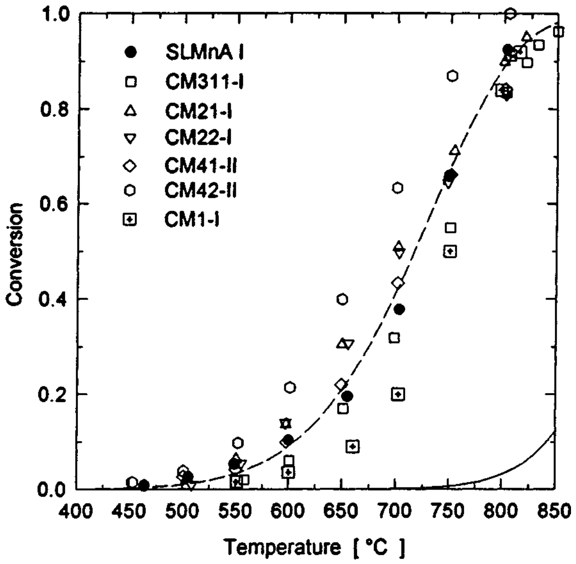

Figure 4. Experimental methane conversions over new catalytic materials calcined 7 h at 1300 °C. (—) represents conversions to carbon dioxide over pumice, (– – –) represents conversions over SLMnA-I. Plug-flow reactor, 2% methane/air, 400 ml/min, 1 g catalyst/10 ml pumice.

apparent activation energies E_{app} and preexponential factors A presented in logarithmic form are summarized in table 3 which also includes calculated specific (k per g) and areal (k' per m^2) kinetic constants for 1000 K (727 °C) (k_{1000} and k'_{1000}) and for 823 K (550 °C) (k_{823} and k'_{823}). These data indicate two important aspects. First, the specific activity (k) seems directly proportional to SSA only up to about 10 m^2/g, as shown in figure 3. Secondly, samples having SSA of about 10 m^2/g and lower approach the same areal activity regardless the preparation method. This dependence of specific activity on SSA confirms that previously observed for samples of $La_{0.66}Sr_{0.34}Ni_{0.3}Co_{0.7}O_3$ perovskite [14,21]. Similarly, this can in part be explained by inaccessibility to the reactants of the SSA corresponding to pores smaller than 10 nm, most likely present in samples of high SSA. It should also be admitted that, in the case of oxides, increase in SSA does not necessarily result in a proportional increase of the active sites.

Thus, although the SLMnA-com seems to withstand much better than the SLMnA-I the short calcination at 1450 °C, in view of areal activities their overall activity can be considered as comparable.

4.3. Catalytic performance of the new materials

Conversion data for the new materials aged at 1300 and 1450 °C are compared with those of SLMnA-I in figures 4 and 5. Selected activity data are also given in table 2. As evident, most of the new perovskites show activity comparable or better than sample SLMnA-I does. Similarly as in the case of SLMnA samples, the conversion data were fitted by the integrated first-order kinetic model also with very good results. The obtained kinetic parameters are listed in table 4. The new transition metal doped refractory perovskites are apparently also more active than recently studied $SrTi_{0.8}Zr_{0.1}Mn_{0.1}O_3$ [29] which was prepared from alkoxides via gel precipitation and calcined at 1000 °C (no time and SSA given [29]). We may surmise that lack of oxygen deficiency and consequently lower oxygen mobility may in part be responsible for the lower activ-

Table 4
Apparent first-order kinetic parameters for the catalytic materials aged 7 h at 1300 °C.

Sample	SSA (m^2/g)	$E_{\rm app}$ (kJ/mol)	$\ln A$ (μmol/(g s bar))	k_{1000} (μmol/(g s bar))	k'_{1000} (μmol/(m^2 s bar))	k_{823} (μmol/(g s bar))	k'_{823} (μmol/(m^2 s bar))
CM311-I	1.4	132	21.0	165	120	5	4
CM21-I	2.0	107	18.6	290	145	19	10
CM22-I	1.3	116	19.6	285	218	14	11
CM41-II	1.4	102	17.8	220	158	18	13
CM42-II	1.9	101	18.1	380	200	28	15
SLMnA-I	4.0	101	17.8	284	71	21	5
SLMnA-com	13	108	19.6	742	57	45	3

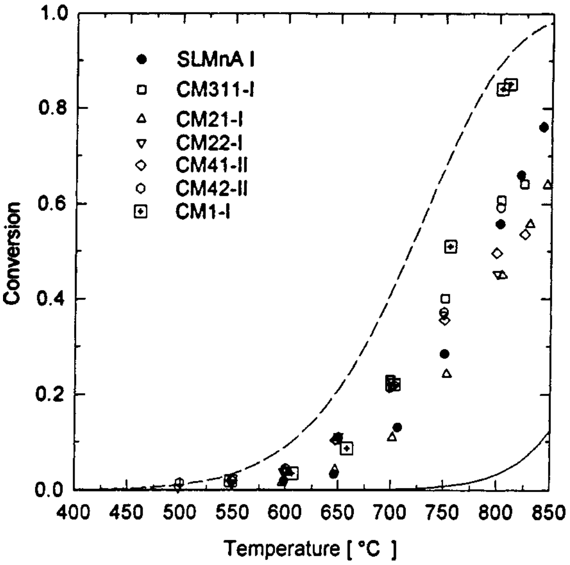

Figure 5. Experimental methane conversions over new catalytic materials calcined 7 h at 1300 °C and 6 h at 1450 °C. (—) represents conversions to carbon dioxide over pumice, (– – –) represents the conversions over SLMnA-I calcined 7 h at 1300 °C. Plug-flow reactor, 2% methane/air, 400 ml/min, 1 g catalyst/10 ml pumice.

ity of $SrTi_{0.8}Zr_{0.1}Mn_{0.1}O_3$. In contrast, while our sample of $SrZr_{0.83}Y_{0.07}Mn_{0.1}O_3$ (CM1-I) perovskite showed at lower temperatures also relatively low conversions, at higher temperatures its activity was comparable to that of other compositions. In fact, CM1-I seems to exhibit the highest thermal resistance, as is clear from figure 4. The CM1-I composition is also far more active than $SrZrO_3$ included here only for comparison (table 2). This illustrates well the role of composition in the activity, but further detailed study is needed to determine its exact effect, specifically of the individual dopants, on the overall performance of a given group of materials.

Although in terms of temperatures of a given conversion and of specific kinetic parameters (per g of catalyst) none of the new materials exhibited as high activity as SLMnA-com, several were very active and their areal kinetic constants k' were actually significantly higher (table 4). Particularly high activity was observed for iron-substituted lanthanum aluminates. Taking into account that neither the new compositions, nor the process of their preparation were fully optimized the obtained results are promising.

One of the desired characteristics of a high-performance combustion catalyst is the absence of carbon monoxide in the effluents. Previous work demonstrated that no carbon monoxide was formed over nickel–cobalt-based perovskites developed for lower combustion temperatures, even when methane-rich mixtures were used [20]. In this work, formation of carbon monoxide was deduced from carbon balance (and later confirmed by GC analysis) at high temperatures over $SrZrO_3$ and over some of the samples aged at 1450 °C, as indicated in table 2. Over $SrZrO_3$ conversion to carbon monoxide $X_{\rm CO}$ was about 15%. Since the formation of carbon monoxide is expected to proceed via gas phase reactions, its presence in the effluents apparently indicates lack of the highly active electron acceptor sites which are expected to be favorably coordinated with active oxygen species. In the case of extensively aged doped perovskites this is reflected also by a very low SSA.

Although 1300 °C seems to be the upper limit for conserving good activity, a number of the new materials could find several practical applications in catalytic combustion technologies operating at temperatures below that limit. These materials might be particularly attractive for catalytic combustion of other hydrocarbons which are activated at temperatures considerably lower than methane. Each composition may exhibit its specific range of thermal stability (temperature of long-term stability, especially in the atmosphere of the combustion effluents) which needs to be determined.

5. Conclusions

The results of the present study clearly indicate that by using proposed criteria, highly active, thermally stable catalytic materials may be designed.

Refractory perovskites substituted with transition metals of low volatility may become active in catalytic combustion. These thermally stable materials can be represented by a common formula $La_{1-x}Sr_xB_{1-y-y'}M_yM'_{y'}O_{3-\delta}$, where B is aluminum, titanium, or zirconium, and M and M′ is the transition metal such as iron, manganese, cobalt, or even nickel, with $y + y' \leqslant 0.2$. Some degree of oxygen deficiency δ needs to be maintained to promote high oxygen mobility and thereby high activity.

The role of specific surface area in the activity of these materials is less important than generally assumed. Thus, while the method of preparation has a significant effect in the formation of highly active sites as well as on their thermal stability and needs to be well controlled, a number of low-cost precursors, properly activated, may be used.

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