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Catalytic activity of powder and monolith perovskites in methane combustion

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Abstract

Honeycomb monolith perovskite catalysts were prepared from ultradispersed powders of mixed oxides of rare-earth metals (La–Ce or Dy–Y) and transition metals (Ni, Fe, Mn) by mechanochemical methods. A plasmochemical method was used to obtain La–Ni containing monoliths. The catalytic activity of powders and monoliths was compared in the catalytic combustion of methane. The intrinsic catalytic properties of the active components (apparent kinetic constant and energy of activation) were not significantly affected by the manufacturing procedure of monoliths in a large range of temperatures. Best performance was exhibited by La–Ni oxides containing monoliths which possess the highest pore volume and fraction of macropores. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The potential advantages of developing a technology based on catalytically supported thermal combustion are very appealing, especially with respect to the prevention of pollutants formation. However, due to the very severe operating conditions, the demands on the catalyst for this application are quite unique. Various catalytic formulations have been proposed in the past decades, as recently reviewed [1].

Moreover, in order to minimize the pressure drop across the catalytic bed, honeycomb monoliths are required, but the interaction of the oxides with washcoats and/or monolithic supports results in a decrease of both catalytic activity and mechanical strength. Materials more durable than cordierite, which is commonly employed for environmental catalytic applications, must be used.

Among different candidate materials perovskites have been proposed for the catalytic combustion of hydrocarbons, but their low specific surface area appears to be a serious disadvantage for their application. In order to increase the specific surface area, various preparation methods have been investigated [2,3]. Perovskites supported on different materials, such as alumina [4] or aluminate spinels [2,4,5], have been also studied.

Mixed oxides of transition and rare-earth metals with perovskite structure are thermally stable in a broad range of oxygen partial pressures and are resistant to poisons [6,7]. Previous work reported on the

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manufacture of ultradispersed powders of mixed oxides of lanthanum and transition metals by plasmochemical and mechanochemical methods [8]. Powder extrusion with subsequent drying and calcination led to monoliths of different geometries [8]. In this work the preparation of powders of active perovskites was extended to different combinations of oxides of transition and rare-earth metals. The activity of monoliths extruded from perovskite powders in the catalytic combustion of methane was measured and compared with that of the active powders.

2. Experimental

2.1. Powders and monoliths preparation

Ultradispersed perovskite powders were prepared by a mechanochemical method starting from oxides or carbonate precursors [9,10]. Mechanical activation of the starting compounds was carried out using high-powered planetary ball mills with an acceleration of ca. 40–60 g and a weight ratio of milling balls to powder of ca. 10:1. After mechanical treatment the powders were annealed for 2–4 h at 900°C. Two series of catalysts, based on La–Ce–M and on Dy–Y–M were thus obtained, M being a transition metal, such as Fe, or Mn, or Ni.

La–Ni perovskite powders were synthesized by a plasmochemical method, injecting mixed nitrite solutions via spray nozzles into the reaction zone of a specially designed reactor equipped with 1–3 arc plasmatrons generating a flux of air plasma with an initial temperature in the range 4000–6000 K [10,11]. The calcination of the resulting powders was performed at 900°C for 1 h.

Honeycomb monolith catalysts were prepared by extrusion of plastic pastes of perovskite powders and additives, such as alumina binder, ceramic fibers, acid peptizer and ethylene glycol. After drying, the monoliths were calcined at 900°C. The optimization of preparation procedures was discussed in [8,9]. The content of active components in the monoliths was 80% by weight.

2.2. Catalysts characterization

Surface areas of active powders and monoliths were measured by the BET method using Ar thermal desorption. Pore volume and pore size distribution were determined by mercury porosimetry using an Auto-Pore 9200 machine.

2.3. Experimental apparatus for catalysts testing

Catalytic activity in methane combustion (T=300–900°C) was determined in a quartz fixed-bed annular flow reactor (18 mm i.d.), heated in an electrical furnace, loaded with 1.5 g of perovskite powder (0.5–1 mm size) or small pieces of monolith (1.2–1.5 g). The monoliths are about 20 mm in average length, 0.9–1.2 mm in wall thickness and include two triangular channels (4.5×4.5×4.5 mm size). Inert quartz particles and glass wool were used as diluent for powder and monolith testing, respectively. Temperature was measured by a K-type thermocouple placed in a quartz tube (5 mm o.d.), coaxial and internal to the reactor. For the catalytic test of monoliths the thermocouple was placed at the exit of the monolith. Gas feeds containing 0.4% CH_4 and 2% O_2 in He, or 1.0% CH_4 in air, obtained by mixing mass flow controlled flows from gas cylinders, were used. Both inlet and outlet gas flows were analyzed by on-line continuous analyzers for CH_4, O_2, CO, CO_2 and NO_x. Before the catalytic tests the samples were treated at 900°C for 1 h in the reaction mixture. In the catalytic experiments the reaction temperature was increased and decreased stepwise, without the conversion data showing any hysteresis. Space velocity was about 60 000 h^{-1}.

3. Results and discussion

3.1. Physical properties of powders and monoliths

Table 1 shows the list of powder samples investigated and the specific surface areas. Perovskite powders with surface areas ranging from 5 to 19 m^2/g were obtained. The surface areas of the Dy–Y containing powders are higher than those of La–Ce containing samples. Carbonate precursors provide higher surface areas than oxide precursors.

In Table 2 characteristic data of specific surface area and porosity of the monolith perovskites investigated are collected. The monoliths exhibited specific surface areas ranging from 46 to 74 m^2/g and

Table 1
Specific surface area (SSA) of perovskite powders

Active component (precursor)	SSA (m^2/g)
La–Ce–Fe (carbonate)	5.3
Dy–Y–Fe (carbonate)	8.6
La–Ce–Mn (carbonate)	19
La–Ce–Mn (oxide)	12
Dy–Y–Mn (oxide)	14
Dy–Y–Ni (carbonate)	9.5
La–Ni (nitrate)	17

porosities from 0.20 to 0.28 cm^3/g. Comparison with the surface area values in Table 1 indicates a different picture in the case of monoliths. This is due to the fact that for each catalyst different formulations of paste were chosen in order to optimize both the rheological properties of pastes and the mechanical strength of monoliths.

In Fig. 1 the cumulative pore volume of monoliths is reported as a function of the pore radius. It appears that, even provided the amount of binder being the same, the different dispersion of all components of the catalyst and the different composition of pastes affect the pore structure. Thus, with nearly identical cumulative pore volumes (about 0.2 cm^3/g for most of the monoliths), the pore size distribution is different. Moreover, in the range of pore radii larger than 5 μm the highest pore volume was found for La–Ce–Mn (O) and the lowest for Dy–Y–Mn (O). With the Dy–Y–Fe catalyst the presence of fibers seems to result in an increase of the ratio between the amount of medium-sized (0.05–1 μm) and small-sized pores (<0.05 μm) without significantly affecting the contribution of larger pores. This also results in an increased specific surface area (74 m^2/g).

A strong effect of preparation method of the powders is observed by comparing the curves of the Ni containing catalysts. La–Ni has nearly twice as much volume within large and medium-sized pores than the Dy–Y–Ni sample, due to a quite different composition of pastes.

These features could affect the catalytic performance under conditions of mass and heat transfer limitations.

3.2. *Catalytic properties of powders and monoliths*

The performance in the catalytic combustion of 0.4% methane with 2% O_2 at 0.09 g s/cm^3 was evaluated for all powder samples. Fig. 2 shows the effect of the reaction temperature on methane conversion. The highest values of conversion were exhibited by the La–Ni sample (10% conversion at about 490°C and 50% conversion at 600°C). Lower conversions were obtained with the systems Dy–Y–M (scale of reactivity: Mn>Ni>Fe) and La–Ce–M (Mn>Fe). In order to assess the possible effect of homogeneous methane combustion, a “blank” test was performed by loading the reactor with quartz powder or quartz wool. The relevant curve reported in Fig. 1 shows that 10% methane conversion was reached at 810°C and 50% at 850°C. In this range of temperatures the conversion of methane in the presence of catalyst approached 100% conversion for the majority of the samples.

The selectivity to CO_2 was very high (close to 100%) for all powdered samples in the range 500–900°C. It must be noticed that in the absence of

Table 2
Specific surface area (SSA) and porosity of perovskite monoliths

Active component (precursor)	Fibers	SSA (m^2/g)	V_{pore} (ml/g)	Fraction of pore (%)	
				>1 μm	>0.1 μm
La–Ce–Fe (carbonate)	+	53	0.20	10	40
Dy–Y–Fe (carbonate)	+	46	0.22	14	36
Dy–Y–Fe (carbonate)	–	74	0.22	5	20
La–Ce–Mn (carbonate)	+	55	0.22	9	41
La–Ce–Mn (oxide)	+	56	0.20	10	35
Dy–Y–Mn (oxide)	+	57	0.21	10	19
Dy–Y–Ni (carbonate)	+	52	0.22	9	32
La–Ni (nitrate)	–	61	0.28	25	43

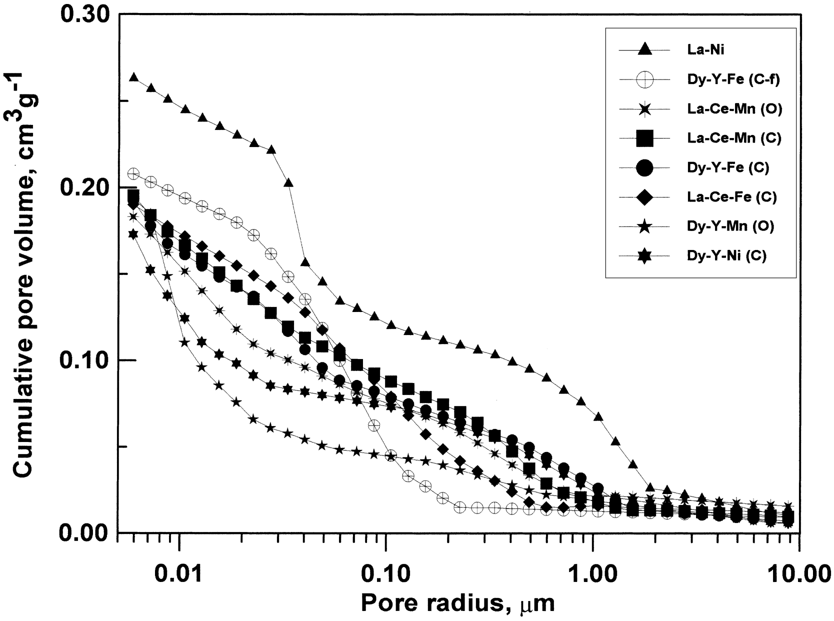

Fig. 1. Cumulative pore volume of monolith catalysts: C=Carbonate precursor; N=Nitrate precursor; O=Oxide precursor; C–F=Carbonate precursor without fibers.

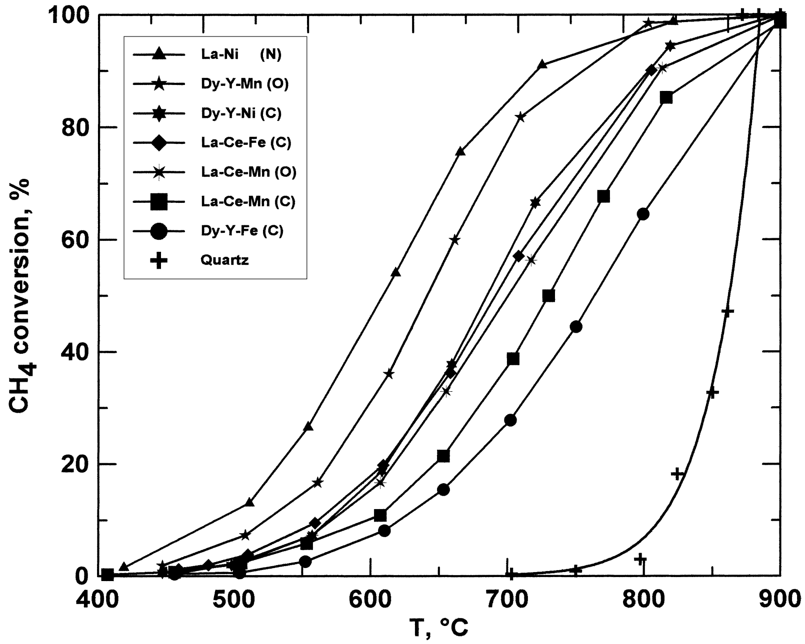

Fig. 2. The effect of temperature on methane conversion for powder catalysts (0.4% CH_4, 2% O_2 in He, SV=60 000 h^{-1}): C=Carbonate precursor; N=Nitrate precursor; O=Oxide precursor; C–F=Carbonate precursor without fibers.

catalyst the selectivity to CO_2 at 800°C was about 50%, due to the significant formation of CO by thermal combustion.

As a first approximation to compare the overall activity of the catalysts a simple model was assumed for the rate of methane combustion:

$$r = kC_{\mathrm{CH}_4},$$

where

$$k = k_0 \exp(-E_a/RT).$$

This relation has been reported for different catalytic systems under the condition of excess oxygen in the feed. Moreover, our preliminary kinetic tests carried out under differential conditions of the reactor have indicated that the reaction order is very close to one in the methane partial pressure. The values of k_0 and E_a, evaluated from the model, are reported in Table 3 together with k values at selected reaction temperatures. The apparent energy of activation was in the range 98–125 kJ/mol, significantly lower than the value obtained for thermal combustion. For Dy–Y containing samples the values of E_a are in the order Fe>Ni>Mn. The values of the corresponding La–Ce containing samples seem to be slightly lower.

The order of the specific catalytic activity and the E_a values for Dy–Y containing samples is the same as found for pure transition metal oxides in the reaction of full oxidation, which has been correlated with the surface oxygen bonding [12]. The higher catalytic activity of the La–Ni plasmochemical sample can be attributed to the high density of extended defects due to preparation procedure. The defects are not annealed upon calcination and laboratory test procedure. The same effect was observed earlier for La–Mn perovskites [11].

In Fig. 3 the values of methane conversion on the monolithic catalysts for the same gas feed composi-

Table 3
Apparent activation energy and kinetic constant values evaluated assuming a first order kinetic equation

Active component (precursor)	E_a (kcal/mol)	k (l/h g)		
		T=500°C	T=600°C	T=700°C
Monoliths in 1% of CH_4 with air				
La–Ni (N)	18.7	16.0	64.6	195.6
La–Ce–Mn (C)	21.0	6.8	32.7	113.3
Dy–Y–Mn (O)	25.2	4.3	28.3	125.5
La–Ce–Fe (C)	26.0	3.3	23.0	107.1
La–Ce–Mn (O)	24.0	2.9	17.7	73.3
Dy–Y–Ni (C)	28.4	2.0	16.9	90.7
Dy–Y–Fe (C)	31.3	1.5	15.3	98.1
Monoliths in 0.4% of CH_4 with 2% of O_2				
La–Ni (N)	18.8	16.0	64.9	197.7
La–Ce–Mn (C)	21.5	5.8	29.1	103.8
La–Ce–Mn (O)	21.5	5.5	25.1	84.3
Dy–Y–Mn (O)	21.0	4.6	22.1	76.8
La–Ce–Fe (C)	26.0	2.4	16.7	78.1
Dy–Y–Ni (C)	27.5	1.6	12.5	63.8
Dy–Y–Fe (C-f)	27.8	1.3	10.6	54.8
Dy–Y–Fe (C)	28.3	1.3	10.5	55.9
Powders in 0.4% of CH_4 with 2% of O_2				
La–Ni (N)	23.5	12.0	69.5	279.4
Dy–Y–Mn (O)	26.1	6.5	45.4	213.0
La–Ce–Fe (C)	25.6	3.5	23.4	106.8
Dy–Y–Ni (C)	28.1	2.6	21.3	112.3
La–Ce–Mn (O)	29.3	2.0	17.4	98.5
La–Ce–Mn (C)	25.4	2.3	15.3	69.1
Dy–Y–Fe (C)	32.6	0.6	6.9	47.7

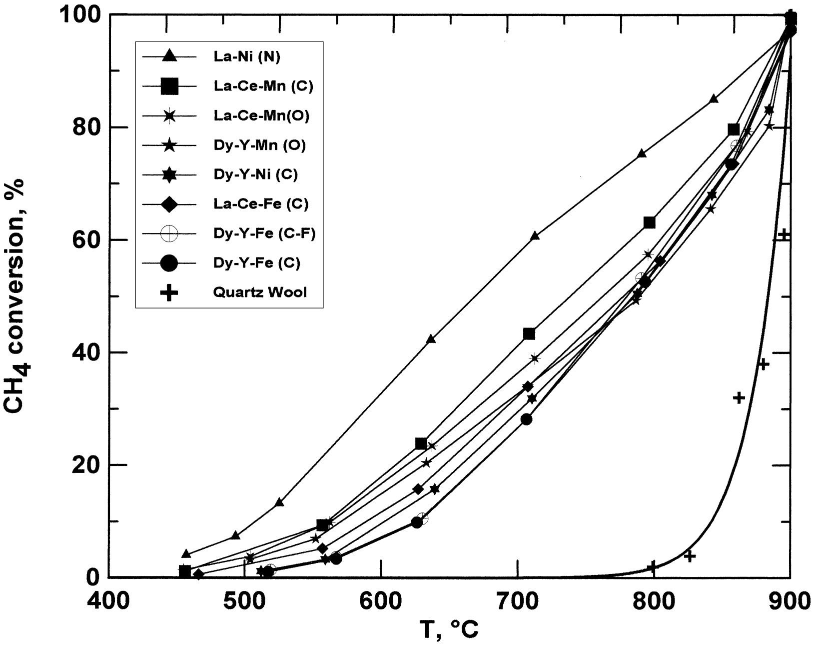

Fig. 3. The effect of temperature on methane conversion for monolith catalysts (0.4% CH_4, 2% O_2 in He, SV=60 000 h^{-1}): C=Carbonate precursor; N=Nitrate precursor; O=Oxide precursor; C–F=Carbonate precursor without fibers.

tion are reported as a function of the reaction temperature. Even in this case the best results were displayed by the system La–Ni (10% conversion at 490°C and 50% at 650°C). Lower and almost similar activities were shown by the other monoliths, Mn-containing samples being relatively more active.

Selectivity to CO_2 was in the range 93–99% for the different monoliths. In the range of the highest temperatures, where the contribution of the homogeneous gas-phase reaction became significant, these values decreased, due to the increasing formation of CO.

The same model assumed for the reaction rate on powder catalysts was used for the monoliths. The calculated values of k_0 and E_a are collected in Table 3 together with k values at selected reaction temperatures. Considering that the values of the energy of activation measured on powders and monoliths are similar, it seems that significant diffusion limitations are not introduced by manufacturing the monoliths from the powders. In the absence of diffusion limitations, one can conclude that the interaction of the active components with alumina is negligible, as was observed in [4], and does not result in any decrease of the specific catalytic activity of active components. Monolith can thus be designed as a porous matrix in which particles of the active components are separated by alumina particles without any significant interaction [8]. In order to better verify these hypotheses, the values of lnk, calculated with respect to the weight of the active components, are plotted against the reaction temperature for the two series of catalysts (Figs. 4 and 5). It appears that the catalytic activities of active components in powdered and monolithic catalysts are very similar within a large range of temperatures. Moreover, for some catalysts the effect of diffusion limitations is indicated by the observation that at T>750°C the straight line overestimates the values of lnk (Figs. 4 and 5). A further indication for diffusion limitation is given by the smaller differences of the catalytic activity among all monoliths with respect to the larger scale of activity of powders. In this respect, the highest activity exhibited by La–Ni containing monolith could be associated with its highest pore volume and fraction of macropores (Table 2).

The effect of feed composition on the performance of monolithic catalysts was investigated by performing catalytic tests with 1% methane in air. In Fig. 6 the effect of the reaction temperature on the methane

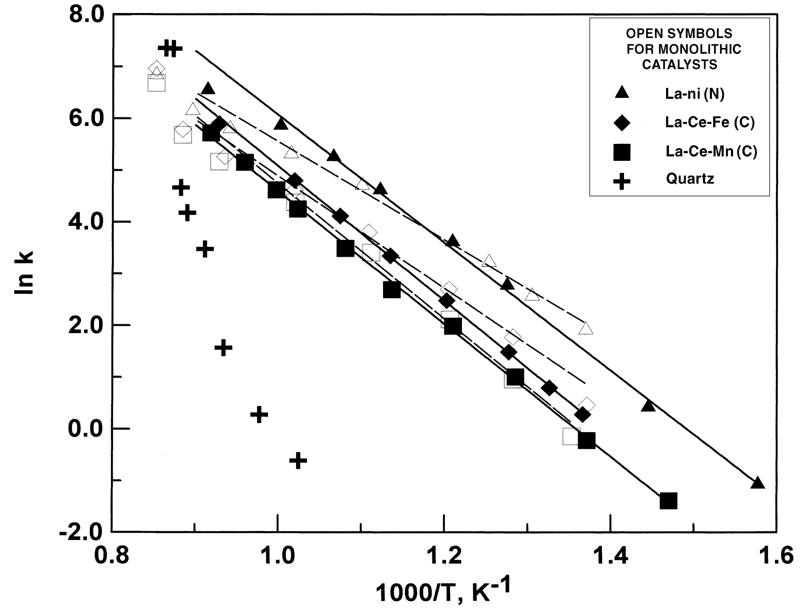

Fig. 4. Arrhenius type plot for La–Ce–M catalysts (0.4% CH_4, 2% O_2 in He, SV=60 000 h^{-1}, open symbols for monoliths): C=Carbonate precursor; N=Nitrate precursor; O=Oxide precursor; C–F=Carbonate precursor without fibers.

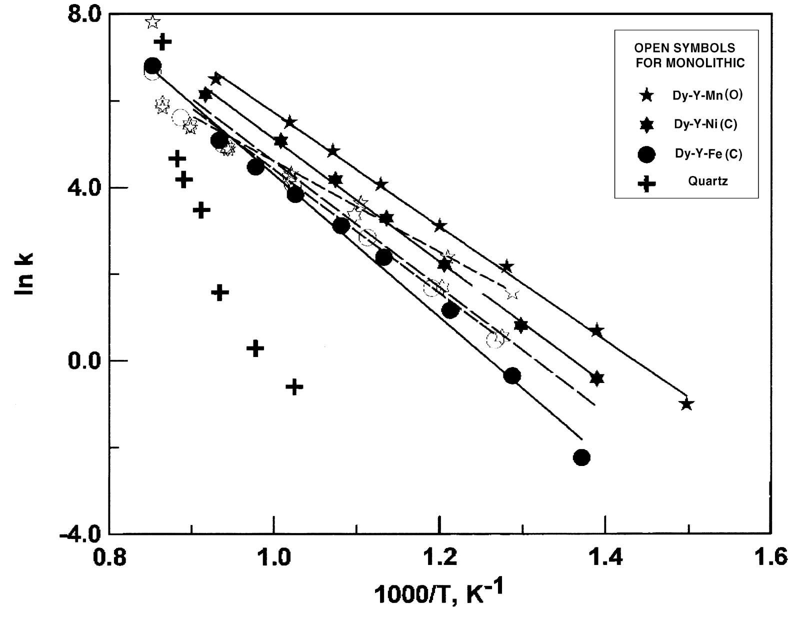

Fig. 5. Arrhenius type plot for Dy–Y–M catalysts (0.4% CH_4, 2% O_2 in He, SV=60 000 h^{-1}, open symbols for monoliths): C=Carbonate precursor; N=Nitrate precursor; O=Oxide precursor; C–F=Carbonate precursor without fibers.

conversion is represented. It must be remembered that under these experimental conditions and in the absence of catalyst the ignition temperature decreased by about 150°C with respect to the 0.4% CH_4, 2% O_2 feed. Moreover, the selectivity to CO increased from about 40% to 60–80%.

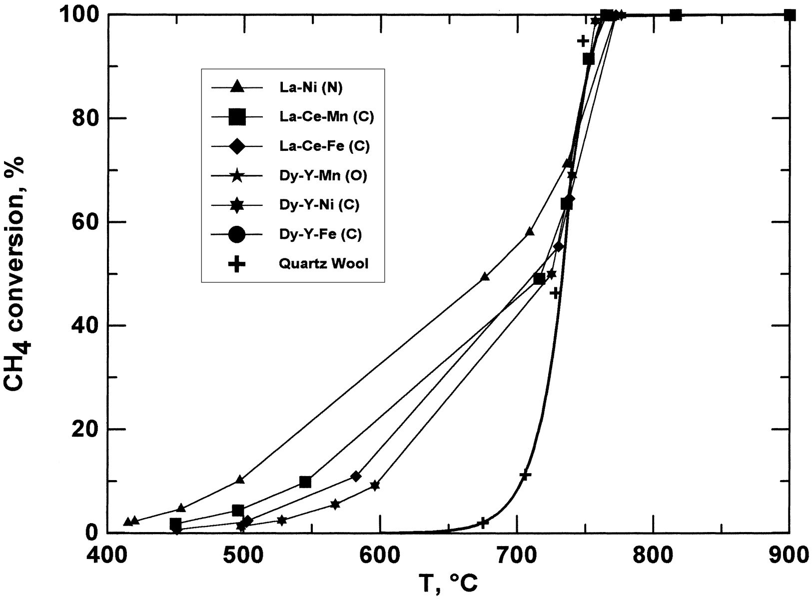

Fig. 6. The effect of temperature on methane conversion for monolith catalysts (1% CH_4 in air, SV=60 000 h^{-1}): C=Carbonate precursor; N=Nitrate precursor; O=Oxide precursor; C–F=Carbonate precursor without fibers.

The values of k_0 and E_a, calculated by the same procedure as indicated above, are collected in Table 3 together with k values at selected reaction temperatures. Comparing the values measured at T<700°C with the two feed compositions, one can conclude that there is a good agreement for the values of k, while the energy of activation for the various monoliths is only slightly affected by the feed composition. At T>700°C homogeneous reactions dominate, the catalytic activity being very similar to that measured with the reactor filled with quartz wool (Fig. 6). At higher methane and oxygen concentrations the selectivity to CO increases, but it is always 2–4 times lower than with the quartz wool-filled reactor. Increasing the concentration of methane and oxygen favors the homogeneous processes, while the presence of catalyst affects only the oxidation of CO.

4. Conclusions

The optimization of the preparation technique allows us to obtain ultradispersed powders of Dy–Y and La–Ce containing mixed oxides with the perovskite structure showing different specific surface areas. These powders can be shaped to thermally stable and mechanically resistant honeycomb monoliths with different porosity characteristics by optimizing the formulation of the pastes.

The monoliths are active and selective in the catalytic combustion of methane, maintaining the catalytic properties of the active components in a large range of temperatures.

The scale of the specific catalytic activities and the apparent energies of activation for monoliths parallel that found for powders. The catalysts decrease the ignition temperature (up to 200°C for $T_{10\%}$), and enhance the selectivity to CO_2 with respect to the uncatalyzed combustion of methane. At T>700–900°C (depending on the feed composition) the gas-phase process becomes predominant for CH_4 activation and under these conditions the catalyst influences only the selectivity to CO/CO_2.

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References

[1] M.F.M. Zwinkels, S.G. Jaras, P.G. Menon, T.A. Griffin, Catal. Rev.-Sci. Eng. 26 (1993) 319.

[2] D.W. Johnson Jr., P.K. Gallagher, F. Schrey, W.W. Rhodes, Am. Ceram. Soc. Bull. 55 (1976) 589.

[3] N. Yamazoe, Y. Teraoka, Catal. Today 8 (1990) 175.

[4] B. de Collongue, E. Garbowski, M. Primet, J. Chem. Soc., Faraday Trans. 87 (1991) 2493.

[5] P.E. Marti, M. Maciejewski, A. Baiker, Appl. Catal. B 4 (1994) 225.

[6] D.L. Trimm, Appl. Catal. 7 (1983) 249.

[7] L.G. Tejuca, J.L.G. Fierro, J.M.D. Tascon, Adv. Catal. 36 (1989) 237.

[8] L.A. Isupova, V.A. Sadykov, S.F. Tikhov, O.N. Kimkhai, O.N. Kovalenko, G.N. Kustova, I.A. Ovsyannikova, Z.A. Dovbii, G.N. Kriukova, Ya. A. Rozovskii, V.F. Tretyakov, V.V. Lunin, Catal. Today 27 (1996) 249.

[9] L.A. Isupova, V.A. Sadykov, L.P. Sovoyova, M.P. Andrianova, V.P. Ivanov, G.N. Kriukova, V.N. Kolomiichuk, E.G. Avvakumov, I.A. Pauli, O.V. Andryushkova, V.A. Poluboyarov, A.Ya. Rozovskii, V.F. Tretyakov, Proceedings of the Sixth International Symposium on Scientific Bases Prep. Heterogeneous Catalysts, Louvain-la Neuve, 5–8 September 1994, vol. 2, p. 231.

[10] V.A. Sadykov, L.A. Isupova, S.F. Tikhov, O.N. Kimkhai, Proceedings of the MRS Fall Meeting, Boston, 28 November–2 December 1994, vol. 386, p. 293.

[11] S.F. Tikhov, V.A. Sadykov, E.A. Pack, O.N. Kimkhai, E.M. Moroz, V.P. Ivanov, G.N. Kustova, G.M. Alikina, Proceedings of the Seventh International Symposium on Heterogeneous Catalysis, Bourgas, 1991, vol. 2, p. 243.

[12] V.I. Marshneva, G.K. Boreskov, React. Kinet. Catal. Lett. 1 (1974) 15.