Available online at www.sciencedirect.com

ScienceDirect

Catalysis Today 117 (2006) 427–432

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Palladium/perovskite/zirconia catalytic premixed fiber burners for efficient and clean natural gas combustion

Stefania Specchia *, Andrea Civera, Guido Saracco, Vito Specchia

Dipartimento di Scienza dei Materiali ed Ingegneria Chimica, Politecnico di Torino–Corso Duca degli Abruzzi, 24-10129 Torino, Italy

Abstract

The present work was aimed at developing and testing – under realistic operating conditions on a specifically assembled pilot plant – a novel generation of catalytic premixed fiber burners for low-environmental-impact natural gas combustion. The adoption of a palladium-$LaMnO_3$-zirconia catalyst developed on purpose, where zirconia acts as a structural promoter and the noble metal/perovskite synergism is effectively exploited, led to enhanced performances with respect to non-catalyzed burners. In particular, lower CO and NO_x emissions were recorded over a wide field of operating conditions (basically excess of air with respect to the stoichiometric condition and nominal heat power).

Also, the effect of ageing and poisoning induced by sulfur compounds added as odorants in the natural gas network was studied, with promising indications as regards the burners durability: the overall performance, in terms of pollutant emissions, appeared to have slightly improved after prolonged exposure to SO_2 and high temperatures.

Keywords: Catalytic combustion; Natural gas; Palladium; Perovskite; Zirconia; Premixed fiber burners

1. Introduction

Reduction of NO_x emissions and increase of safety and efficiency in the natural gas combustion process have recently become even more important since the demand of natural gas as an energy source has been increasing worldwide. Catalytic combustion of natural gas has been attracting attention since the mid-1970s when natural gas came to be used worldwide, and various kinds of application concepts have been proposed [1,2]. Premixed catalytic combustion can indeed guarantee the lowest NO_x emissions compared to other combustion technologies, as detailed in Fig. 1. In response to modern climate policy requirements, the increasing use of methane as a source of thermal energy has promoted a great effort to develop new highly efficient and clean combustion appliances [3]. Over the last decade, premixed combustion within porous media has been the object of extensive theoretical and experimental research [4], in view of its great potential in enhancing the heat transfer efficiency and reducing the environmental impact. This technology entails a more intense heat exchange by radiation and conduction from the solid to the heat sink, with an increase in the overall thermal efficiency and a reduction of flame temperature, which results into a limited production of thermal NO_x. The performances of premixed burners can be further improved by adopting perovskite-based catalysts [5,6], the presence of which can increase the fuel flow rate fraction burnt within or just downstream the burner surface, thus maximizing the heat fraction transferred by radiation, cooling the flame and favoring the combustion completion with lower CO and unburned hydrocarbons emission levels [7].

In the present work, FeCrAlloy fiber-mat burners were catalyzed by means of an ad hoc developed deposition technique based on solution combustion synthesis (SCS) [8]. An optimized pre-treatment that favors the formation of an α-Al_2O_3 layer on the fibers surface was designed, both to protect the metal alloy from further oxidation when the burner is operated and for optimal catalyst anchoring purposes. SCS operating conditions on the FeCrAlloy fiber mats were adjusted and tailored in order to find the best compromise between adhesion and specific surface area of the deposited catalyst layer.

A zirconia-stabilized perovskite catalyst was chosen, in line with earlier investigations, and an attempt was made to exploit the potential synergism with palladium [9]. Zirconia acts as a structural promoter, in that its presence limits the specific

---

* Corresponding author. Tel.: +39 011 5644608; fax: +39 011 5644699.
E-mail address: stefania.specchia@polito.it (S. Specchia).

0920-5861/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2006.06.041

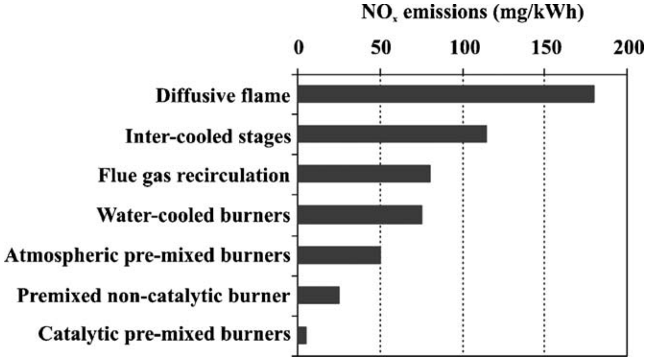

Fig. 1. Potential NO_x emissions achievable with different burner technologies (courtesy of Viessmann GmbH).

surface area loss caused by prolonged exposure to high temperatures [10]. Moreover, the potential benefits of zirconia as support to enhance the temperature stability of $LaMnO_3$ perovskite has been broadly demonstrated [11]. Dispersing a noble metal over a support like perovskite, intrinsically active towards methane oxidation, is expected to have favorable effects on the overall catalytic activity.

2. Experimental

Two different catalytic fiber burners were prepared by using commercial knitted fiber mats (Acotech NIT 200/S) made of FeCrAlloy. Panels were firstly kept at 1200 °C for 10 min under a flow of oxygen (0.5 vol% in N_2) so as to favor the regular growth of the alumina grains into a uniform protective layer and ensure a good adherence of the catalytic phase to be deposited on the metallic mat [12]. Subsequently, the $LaMnO_3{\cdot}2ZrO_2$ catalyst (burner A) and the $Pd/LaMnO_3{\cdot}2ZrO_2$ system (burner B) were deposited via SCS-spray pyrolysis. For the preparation of burner A, an aqueous solution of the perovskite/zirconia precursors was sprayed over the surface of the FeCrAlloy panel, previously heated at 400 °C. Due to the in situ pyrolysis/combustion synthesis occurring on the hot panel surface, catalyst formation was obtained. The panel was then placed back into the hot oven to stabilize the coating. The spray deposition cycle was repeated several times in order to achieve the desired catalyst load (namely 2%, w/w). For a further stabilization and complete crystallization of the catalytic phase, the burner was finally calcined at 900 °C for 2 h in still air. The preparation of burner B was done following the same procedure used for burner A. One additional step was introduced for the palladium deposition; this was carried out by means of a further spray-pyrolysis run performed over the perovskite/zirconia layer, by employing a diluted $Pd(NO_3)_2$ aqueous solution. Calcination at 600 °C followed, in order to promote the full decomposition of palladium nitrate into the oxidized form PdO.

Tests under realistic operating conditions were performed on a partially modified commercial condensing boiler rig. Methane was fed to a modulating electro-valve, by means of which its volumetric flow rate could be varied (max. power ~50 kW). Air coming from a blower was mixed with methane in a Venturi positioned so that a proper mixing was achieved before entering the burner. The fiber mat burner, fitted vertically in the boiler, fired horizontally through the heat exchanger coils. Tests were carried out over a wide range of operating conditions by varying the nominal power Q [kW] and the air excess E_a [%]. A K-type thermocouple measured the temperature on the downstream surface of the panel (the burner deck).

Depending on the thermal/physical properties of the porous media, as well as on the operating conditions, three different combustion regimes can be established [5]: the *radiant*, the *transition* and the *blue-flame* modes. The combustion regime established on the burner was assessed by direct observation through a suitable peep hole.

The flue gases composition (O_2, CO_2, CO and NO) was monitored by means of a multiple gas continuous analyzer (from ABB). Tests were performed both on 'fresh' burners and after an accelerated ageing/poisoning treatment. Since Pd/perovskite-based catalysts are prone to poisoning induced by sulfur compounds (normally used as odorants for natural gas networks), the catalyzed panels were kept in an electric oven at 800 °C under a nitrogen flow containing 200 ppmv of SO_2, chosen several times greater than the odorant concentration added to commercial natural gas (about 8 ppmv, in Italy, as THT) so as to accelerate any possible poisoning effect. The burners were subsequently tested after 24 h, 48 h, 96 h, 168 h (1 week), 336 h (2 weeks) and 504 h (3 weeks).

SEM analyses, coupled with EDS, were also carried out on samples cut from burners, in order to assess whether exposure to sulfur and high temperatures had influenced the catalytic layer morphology.

3. Results and discussion

Fig. 2 compares the areas of the different regimes of the burners A and B together with their non-catalytic counterpart. For specific heat power values q_s lower than about 1900 kW/m^2, catalyzed burners could maintain flameless combustion at air excess (E_a) values higher than those of the non-catalytic counterpart, while for q_s higher than 1900 kW/m^2, the

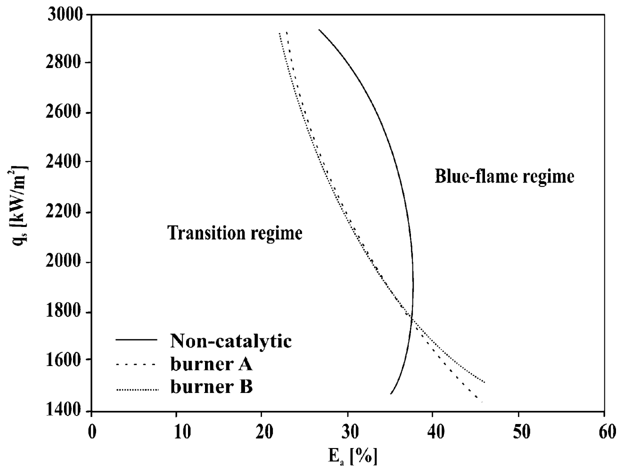

Fig. 2. Combustion regimes map for burners A and B and their non-catalytic counterpart.

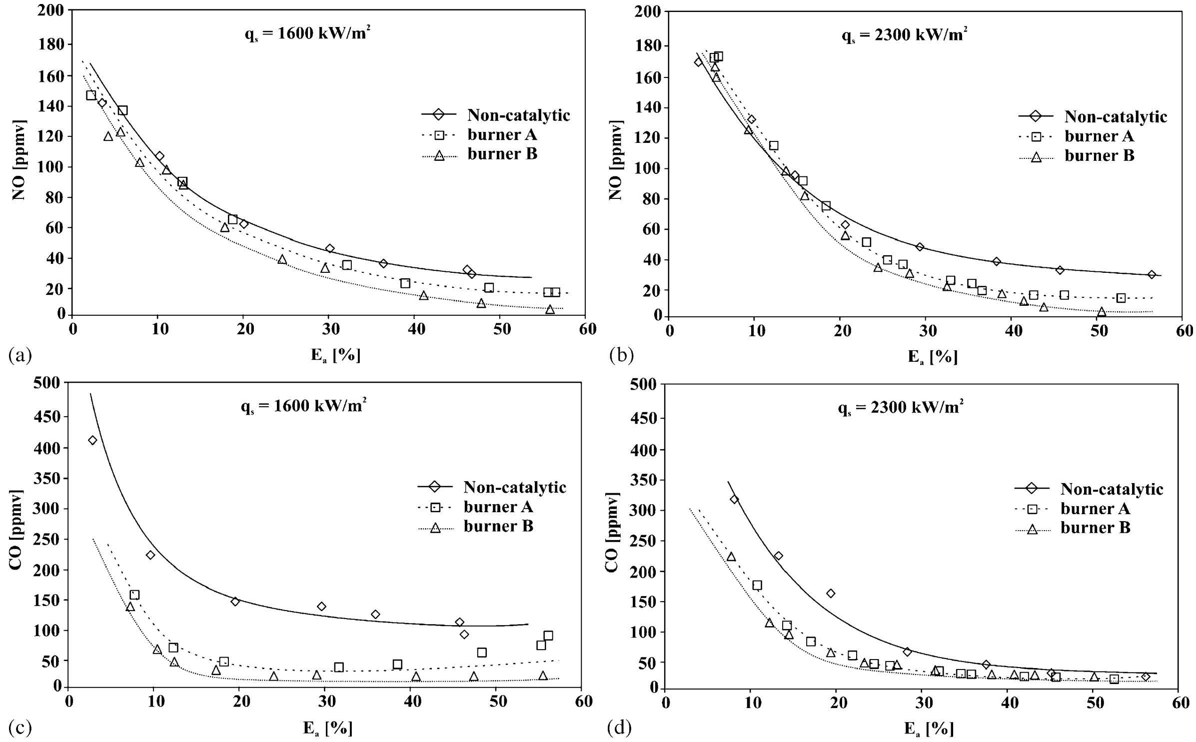

Fig. 3. NO (a–b) and CO (c–d) emissions [ppm] at different q_s vs. E_a for burners A and B and their non-catalytic counterpart.

catalyzed burners shifted into the transition regime at lower E_a values, with respect to the non-catalyzed burner. A complete radiant regime was never reached due to a technical limitation of the test rig, unable to go below the specific power of 1400 kW/m^2.

The importance of two opposite phenomena could explain this behavior. On the one hand, the deposited catalyst reduces the panel overall porosity, thus increasing the gas path tortuosity. Especially at high temperatures, the gas expansion combined with the reduced porosity results in an enhanced local gas momentum, which pushes the flame outside the burner deck. On the other hand, the presence of the catalyst can stabilize at least part of the flame front within the porous media by promoting the completion of methane oxidation. At lower q_s, the latter phenomenon prevailed: methane combustion was more effectively assisted by the catalyst as a result of a higher residence time inside the burner and an E_a increase did not cause an immediate shift into the transition mode. At high powers, instead, the combustion mode could easily shift from the transition to blue-flame regime, owing the prevalence of the former phenomenon. Moreover, the local gas momentum was further enhanced by the E_a increase.

With the catalyst promoting complete methane oxidation, a greater portion of the combustion heat can be released within the porous medium, thus increasing its radiant output and the overall thermal efficiency. If the catalyst can stabilize the combustion reactions deeper inside the metal fiber mat, the homogenous gas phase is cooled by the porous medium that absorbs and radiates directly to the heat sink part of the combustion heat released. Thermal NO_x emissions, generated according to the Zeldovich mechanism [13], are expected to be lower with lower flame temperatures. This was indeed confirmed by the experimental results: Fig. 3a and b show how the catalyzed burners A and B could generally lower the NO levels with respect to the non-catalytic counter part. The beneficial effect of the catalyst was slightly more evident at higher E_a values: E_a equal to around 30%, for instance, the catalyst could reduce the NO emissions of about one-third with respect to the non-catalytic burner, nearly independently of the input power. The presence of Pd on burner B seems to further enhance the catalytic performance especially for E_a greater than 20%. When the air-to-fuel ratio is decreased, two phenomena interact: the contact time between the oxygen and nitrogen species is higher, yet the oxygen partial pressure is lower. These two phenomena influence NO generation from opposite sides [13], thus leading often to higher concentrations of nitrogen oxides.

As concerns CO emissions, when E_a approaches the stoichiometric condition, the non-catalytically assisted combustion is strongly penalized, while in the presence of the catalyst those unacceptable CO emissions could be lowered significantly (see Fig. 3c and d). For instance, for E_a equal to 10%, over the whole range of Q considered, the catalyzed burners could reduce CO to 50 ppmv, whereas the non-catalytic burner produced CO over 300 ppmv. In the case of CO emissions, the effect of the Pd addition (burner B) was practically negligible.

Anyway, for both CO and NO emissions, the synergetic effect of Pd on perovskite/zirconia is effectively exploited, perfectly in line with the experimental data reported in literature [9], where the same catalysts were testes as powder: the performance of Pd/perovskite/zirconia was superior (lower

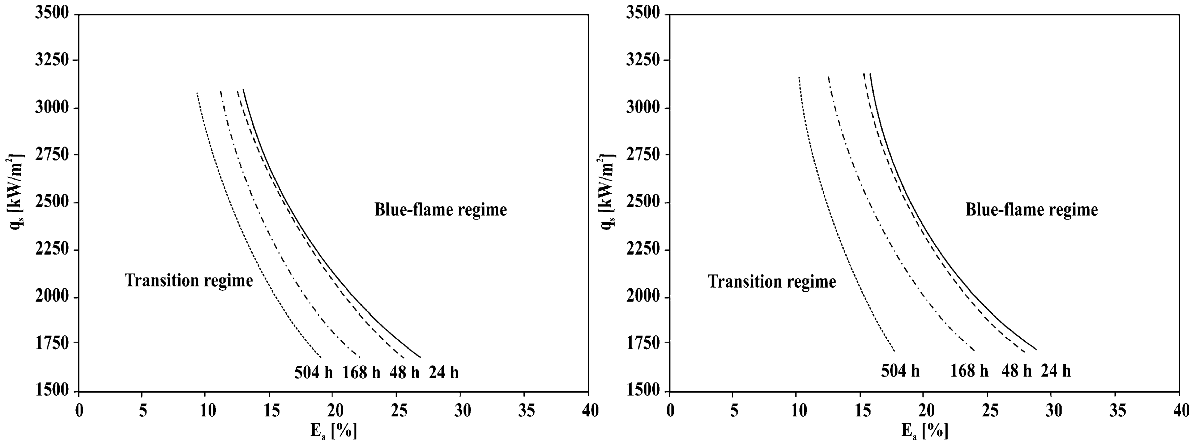

Fig. 4. Combustion regimes map evolution upon prolonged poisoning: burner A (left) and burner B (right).

T_{50} values were reached) compared to Pd/zirconia or Pd/perovskite catalysts. In the literature, there is a general agreement on PdO formation under oxygen-rich reaction conditions [14]; a synergetic effect between the metal phase and the zirconia support itself has been claimed [14,15]. Since methane combustion occurs only at high temperature (more than 800 °C), all Pd is converted in PdO [16]; the improved catalytic activity is probably due to a very high dispersion of the PdO crystals [17]. In all the experimental runs carried out on the domestic boiler rig, the temperature of the burner surface, measured via a thermocouple simply touching the surface itself, was always above 800 °C: usually the shift from the blue flame to the transition regime occurs between 950 °C and 1050 °C. The temperature excursions across the temperatures at which PdO decomposition to Pd occurs (900–1000 °C) makes it rather difficult to predict precisely the activity of the Pd catalyst in the various locations of the burner and its actual contribution to the overall burner performance, mostly because it should strongly depend on the "history" of the catalyst itself.

The effect of poisoning on catalytic burners is presented in Fig. 4; for both burners A and B, prolonged exposure to SO_2 caused shrinkage of the transition regime zone. This effect might be due to the morphological modification of the fibers burner surface that could in some extent cause a reduction of the local void fraction which allowed the same local gas momentum intensity with decreased flow rates. This notwithstanding, the

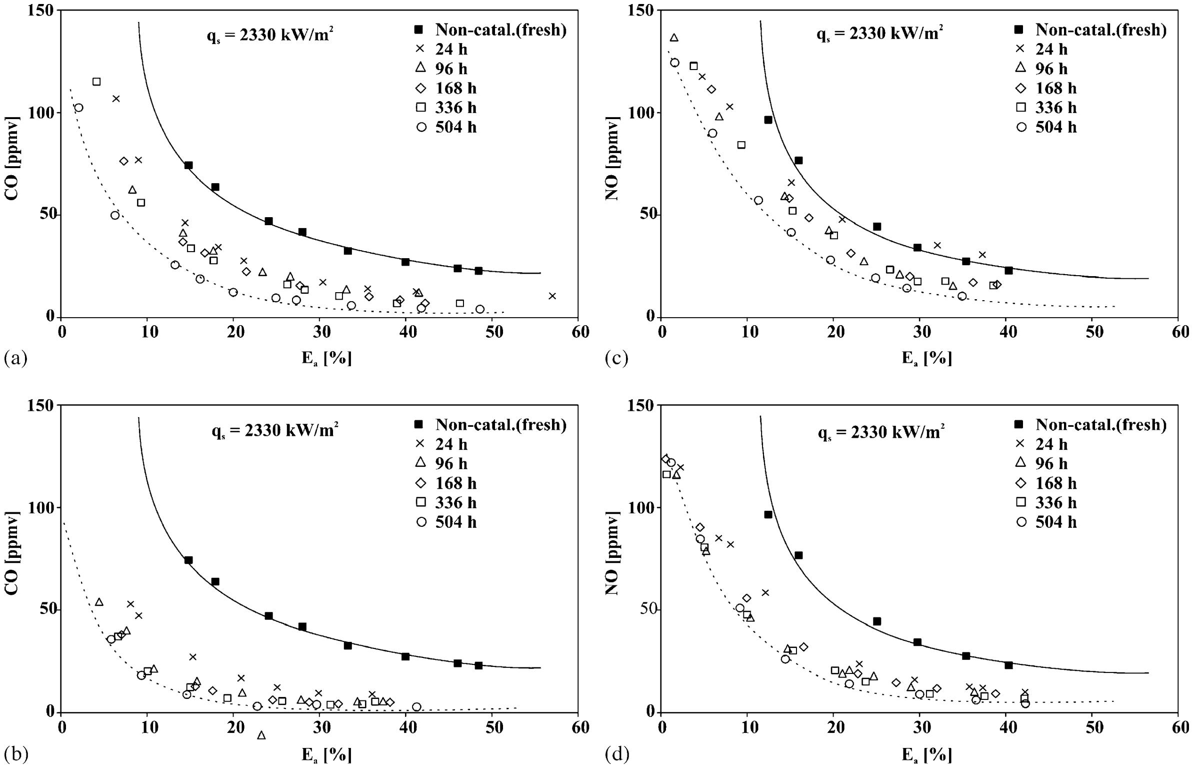

Fig. 5. Pollutant emissions at 2.330 kW/m^2, after prolonged exposure (24 h, 96 h, 168 h, 336 h and 504 h) to SO_2: (a) CO emissions over burner A, (b) CO emissions over burner B, (c) NO emissions over burner A and (d) NO emissions over burner B.

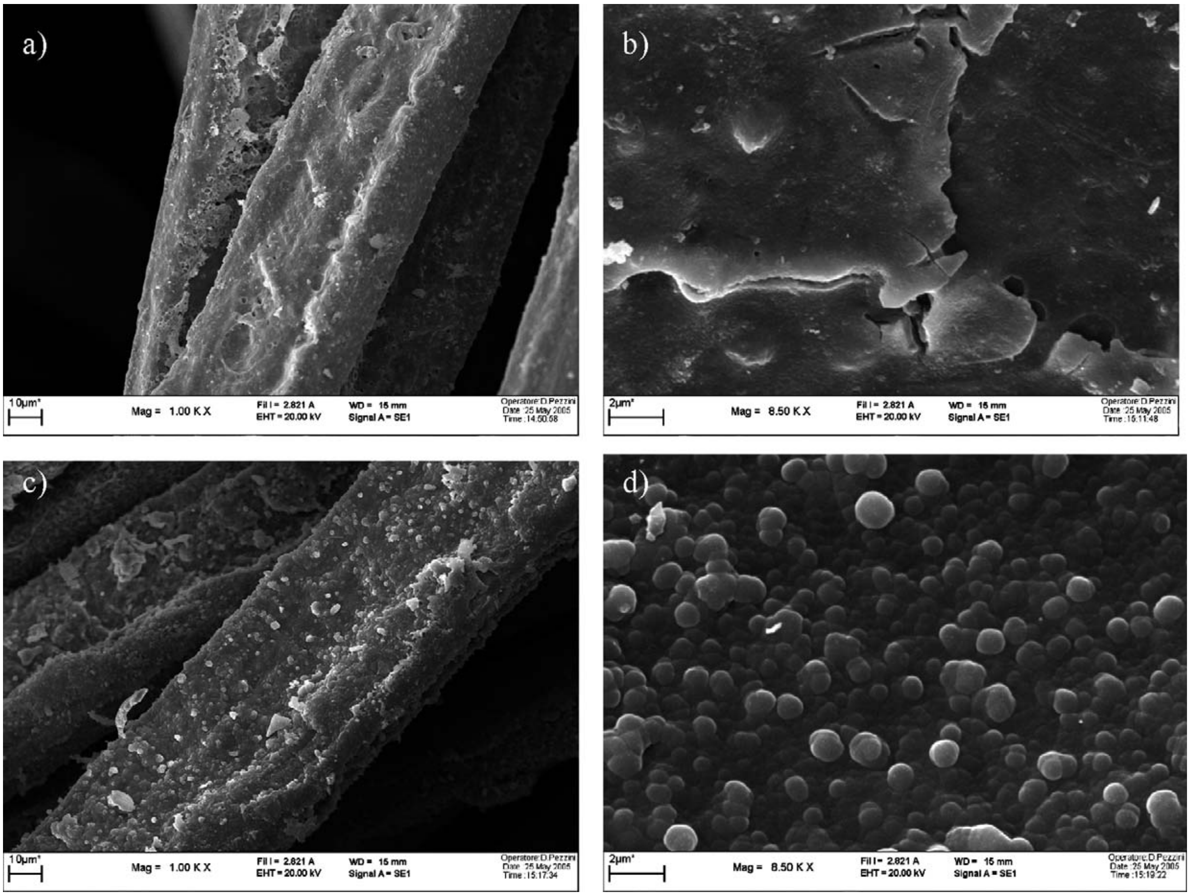

Fig. 6. SEM micrographs of Pd/$LaMnO_3 \cdot 2ZrO_2$ deposited over FeCrAlloy fibers after 1 week (a and b) and 3 weeks (c and d) of ageing/poisoning.

catalyst could always reduce CO and NO emissions with respect to the non-catalytic counterpart and, more interestingly, a slight improvement was found in the overall performance of catalyzed burners for higher and higher operating time (see Fig. 5).

Fig. 6 shows how the morphology of the catalytic layer changed upon ageing/poisoning. While after 1 week (Fig. 6a and b) the burner fibers are covered with a rather uniform catalytic layer, the surface of which appears to be homogenously rough, with irregularly scattered protuberances and cracks, a radically different morphology can be observed on the sample treated for 3 weeks (Fig. 6c and d). In particular, the evolution of the superficial roughness into a uniformly distributed globular structure might explain, to a certain extent, the improved catalytic performance in view of an enhanced interaction with the gaseous reagents. Further analyses are however required to gain a better understanding of the reasons behind this behavior.

4. Conclusions

The catalyst composition chosen and the deposition technique developed allowed the design of premixed metal fiber burners with very interesting performances, in that they were able, over a wide field of operating conditions, to give limited pollutant emissions, both in terms of CO and NO_x. Even more interesting are the durability and resistance to sulfur poisoning. Given the SO_2 concentration chosen, conservatively more than 20 times greater than the real THT concentration employed for the methane network in Italy, the results obtained in this work seem to guarantee that the $LaMnO_3 \cdot 2ZrO_2$ (+Pd) catalytic system can still contribute to an environmentally cleaner combustion – with respect to a non-catalytic burner – after as long as an equivalent year of operation.

Acknowledgements

Funding from the European Union is gratefully acknowledged (EU project CAT-NAT nr G5RD-CT2001-00567: cost-effective and durable nanostructured Pd catalysts for natural gas vehicle and premixed burners applications).

References

[1] H. Sadamori, Catal. Today 47 (1999) 325.
[2] M. Lyubovsky, H. Karim, P. Menacherry, S. Boorse, R. LaPierre, W.C. Pfefferle, S. Roychoudhury, Catal. Today 83 (2003) 183.
[3] P. Forzatti, G. Groppi, Catal. Today 54 (1999) 165.
[4] G. Saracco, I. Cerri, V. Specchia, R. Accornero, Chem. Eng. Sci. 54 (1999) 3599.
[5] I. Cerri, G. Saracco, V. Specchia, D. Trimis, Chem. Eng. J. 82 (2001) 73.
[6] L. Marchetti, L. Forni, Appl. Catal. B 15 (1998) 179.

[7] J.G. McCarty, H. Wise, Catal. Today 8 (1990) 231.

[8] S. Specchia, A. Civera, G. Saracco, Chem. Eng. Sci. 59 (22–23) (2004) 5091.

[9] A. Civera, G. Negro, S. Specchia, G. Saracco, V. Specchia, Catal. Today 100 (2005) 275.

[10] C.A. Müller, M. Maciejewski, R.A. Koeppel, A. Baiker, J. Catal. 166 (1997) 36.

[11] S. Cimino, R. Pirone, L. Lisi, Appl. Catal. B 35 (2002) 243.

[12] D. Ugues, S. Specchia, G. Saracco, Ind. Eng. Chem. Res. 43 (2004) 1990.

[13] J.A. Miller, C.T. Bowman, Prog. Energy Comb. Sci. 15 (1989) 287.

[14] P. Gélin, M. Primet, Appl. Catal. B 39 (2002) 1.

[15] D. Ciuparu, E. Altman, L. Pfefferle, J. Catal. 203 (2001) 64.

[16] M. Faticanti, N. Cioffi, S. De Rossi, N. Ditaranto, P. Porta, L. Sabbatici, T. Bleve-Zacheo, Appl. Catal. B 60 (2005) 73.

[17] D. Ciuparu, M. Lyubovsky, E. Altman, L.D. Pfefferle, A. Datye, Catal. Rev. 44 (2002) 593.