Ageing Mechanisms of $Pd/CeO_2 \cdot 2ZrO_2$ Catalyst for Natural Gas Combustion

P. Palmisano[1], L.D. Vella[1], S. Specchia[1], E. Finocchio[2], G. Busca[2], G. Saracco[1]

1. Politecnico di Torino, Dip. di Scienza dei Materiali e Ing. Chimica - Torino - ITALY.
2. Università di Genova, Dip. di Ing. Chimica e di Processo "G.B. Bonino" - Genova - ITALY

1. General aspects

In the last decades, the growing importance of natural gas (NG) as a power source increased the efforts to develop efficient and safe combustion systems. Promising results were obtained with low-environmental-impact premixed metal fibre burners, due to their thermal efficiency and environmental impact superior performance (remarkable NO_x reduction [1]). Coupling radiant-premixed burners with PdO_x-based catalysts proved to further improve burners' performance. With such catalysts (attractive for their low cost, thermo-chemical stability at high temperature (900-1100°C) and catalytic activity [1]) the fuel fraction burnt within or just downstream the burner outlet surface is increased, thus maximizing the radiant heat fraction, cooling flame temperature and improving combustion completeness (lower CO and unburnt HC [2]). Since PdO_x-based catalysts are prone to be poisoned by S-compounds [2], used as odorants in NG networks, the present work deals with a deep analysis on poisoning mechanisms induced by S-compounds on 2% $Pd/CeO_2 \cdot 2ZrO_2$ in order to assess catalysts with longer lifetime.
The mixed oxide system of CeO_2-ZrO_2 is very promising in fact, ZrO_2 acts as a structural promoter, in that its presence limits the specific surface area losses caused by prolonged exposure to high temperatures [3]; CeO_2 is particularly appreciated as promoter for many utilizations in the catalytic combustion with noticeable application as automotive exhausts oxidation catalyst. Ceria shows, in fact, a good capability of changing rapidly its oxidation number from Ce^{3+} to Ce^{4+} state, with a consequent fast release of oxygen from its lattice to the close species [4, 5]. The production of ceria nanoparticles by combustion synthesis, is also widely studied since 1990 [6], with a particular attention to obtain high surface area values [7]. The CeO_2-ZrO_2 production by co-synthesis is seen as a good method that should give a catalytic material with higher thermal stability respect to the simple oxides.

2. Experimental

2.1. Catalysts preparation

2% $Pd/CeO_2 \cdot 2ZrO_2$ supported catalyst was prepared by the Solution Combustion Synthesis method, a process based on the oxidation of an organic fuel, like glycine, which provides the necessary synthesis heat [1,2]. Metal nitrates of Ce, Zr and Pd (Aldrich, 99% purity) were used as precursors, acting as oxidizers of glycine in solution. The organic molecule plays a double role: it reacts with the precursors (metal nitrates) and, by forming complexes with metal cations in aqueous solution, it guarantees good solution homogeneity, preventing the preferential precipitation of ionic species. The overall combustion reaction can be written as:

$$Ce(NO_3)_3 + 2ZrO(NO_3)_2 + Pd(NO_3)_2 + {}^{38}/_5 COOH\text{-}CH_2\text{-}NH_2 + {}^{28}/_5 O_2 \rightarrow$$

$$Pd(CeO_2 \cdot 2ZrO_2) + {}^{76}/_5 CO_2 + 19H_2O + {}^{83}/_{10} N_2 \qquad (1)$$

The precursors and fuel, dosed in the stoichiometric amount, were dissolved in distilled water and the resulting solution, thoroughly stirred to ensure complete dissolution of all reagents, was then transferred in a ceramic shell placed into an electric oven set at 450°C. After water evaporation and a significant increase in the system viscosity, the heat released in the fast reactions allowed the formation of the catalytic powder. Subsequently, the latter was calcined in oven at 800°C for 2 hours in still air [2].

2.2. Ageing procedure

Since Pd/oxide-based catalysts are prone to be poisoned by sulfur compounds (normally used as odorants in natural gas networks), the catalytic powder was kept in an electric tubular oven at 800°C (a thermocouple was used to monitor the furnace temperature) under a flow rate with typical domestic boiler exhaust composition (9% CO_2, 18% H_2O, 2% O_2 in N_2); 200 ppmv of SO_2 were added too. The latter value was chosen several times higher than the odorant supplementary concentration in commercial natural gas (about 8 ppmv, in Italy, as THT) so as to accelerate any possible poisoning effect [8-10]. Earlier sulfur poisoning studies on perovskite catalysts showed that the basic poisoning mechanism under catalytic combustion conditions was chemisorption of SO_2/SO_3 species generated by combustion of whatever sulfur-organic compound present in the feed (e.g. odorants) [10]. Particularly, it was demonstrated that the direct presence of SO_2 or of the THT odorant in the feed did not lead to a significantly different ageing effect, provided the overall sulfur content remaining the same. SO_2/SO_3 species, in fact, resulted from the total oxidation of S-containing organics during the combustion process [11]. For this reason only ageing runs with a SO_2-laden flow were accomplished. The catalyzed burners were continuously aged up to 3 weeks: for a domestic boiler, such operating time in 200 ppmv SO_2 atmosphere may be considered equivalent to an utilization life time of approximately three years under real operation.

2.3. Catalyst characterization

The fresh and poisoned catalytic powders were characterized by X-Ray diffraction analysis (PW 1710 Philips diffractometer equipped with a monochromator Cu K□; markers located according the PcpdfWin database) to assess their purity and crystalline structure. The BET surface area was evaluated from the linear parts of the BET plot of the N_2 adsorption isotherms (Micromeritics ASAP 2010 analyzer). Scanning Electron Microscope (FESEM Leo 50/50 VP with Gemini column) was employed to analyze the microstructure of the crystal aggregates. Temperature Programmed Oxidation-Desorption tests (Thermoquest TPD/R/O 1100 Series, Thermo Finningan analyzer, equipped with a thermal conductivity detector TCD) were employed to investigate the O_2 desorption with temperature. Infrared spectroscopy (Nicolet Nexus FT instrument) was also assessed: pure catalyst powders were pressed in self supporting tablets (20 mg average weight) and treated in vacuum at several temperatures in IR cell connected to a gas management apparatus. Fresh and aged catalysts were out-gassed at 500°C and cooled at liquid N_2 temperature before CO adsorption. 10 torr of CO were introduced in the IR cell to saturate catalysts surface sites. IR spectra were recorded from –130°C to room temperature. In the spectra of adsorbed CO, the activated surface was subtracted. The catalytic activity towards NG oxidation of the fresh and aged catalytic powders was tested in a lab-scale fixed-bed micro-reactor (Temperature Programmed Combustion TPC): 0.1 g of catalyst mixed with 0.9 g of SiO_2, sandwiched between two quartz wool layers, were inserted in a quartz tube (4 mm ID). The obtained micro-reactor was placed into a PID regulated electrical oven [12] and fed with 50 Ncm^3/min of a gaseous mixture containing 2% CH_4 and 16% O_2 in He. The micro-reactor temperature was measured by a K-thermocouple placed inside the catalytic bed. Starting from 800°C, the oven temperature was decreased at 2°C/min rate and the outlet CO_2, CO, CH_4 and O_2 concentrations were determined by a continuous analyzer, thus allowing to evaluate CH_4

conversion. The half-conversion temperature (T_{50}) was considered as an index of the powders catalytic activity.

3. Results and discussion

3.1. Activity towards CH_4 combustion

The fresh catalyst powder prepared via SCS crystallized as $Ce_2Zr_3O_{10}$ in the tetragonal system, to respect the stoichiometry (CeO_2:ZrO_2 = 1:2); it is possible to observe in the XRD patterns of Fig. 1 the ZrO_2 phase that segregated out to the main tetragonal system. The aged catalysts preserved the crystalline structure obtained after SCS synthesis with an increasing presence of a cubic CeO_2 phase that segregated from the reference initial tetragonal crystalline structure. The phenomenon is well distinguishable after 3 weeks (3W sample) of ageing treatment. The Pd presence (2% w/w) was not detected because this element was under the detection threshold, as well as the presence of other species related to the carbonation/sulfur or hydrothermal ageing.

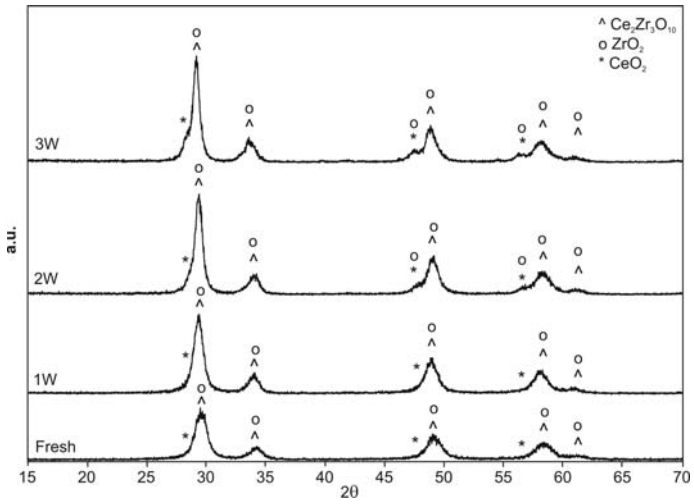

Fig. 1 XRD patterns for 2% $Pd/CeO_2{\cdot}2ZrO_2$ catalysts in fresh and aged samples (1 week: 1W; 2 weeks: 2W; 3 weeks: 3W).

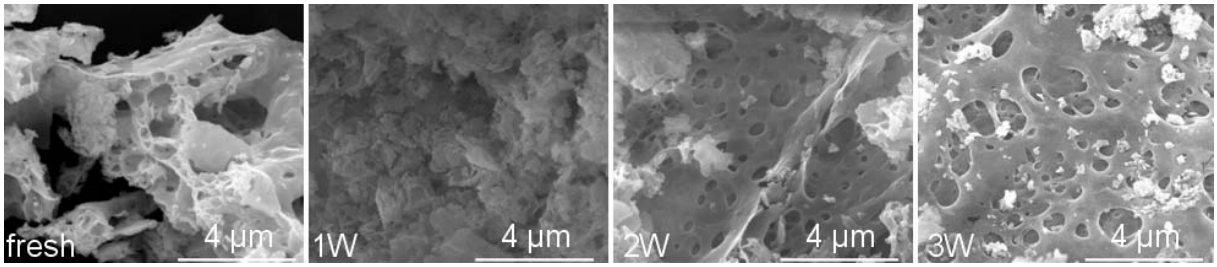

Fig. 2 FESEM images for 2% $Pd/CeO_2{\cdot}2ZrO_2$ in fresh and aged status (25kX).

The FESEM images reported in Fig. 2 show that the fresh powder explained a spongy structure with pores of about 1 µm in diameter. After 1 week of treatment, the morphology changed radically exhibiting a notched surface. Sintering phenomena occurred after 2 weeks of ageing; 2W and 3W samples showed a smooth surface with micro porosity in a range of about 1µm.

Fig. 3 shows all the TPC results of fresh and poisoned $Pd/CeO_2{\cdot}2ZrO_2$: the performance

remained stable till 1 week, with a decline increasing with time after 2 weeks. T_{50} was about 385°C for both fresh and 1W sample but got down to 420°C and 490°C for 2W and 3W sample, respectively. Only the 1W sample reached the complete CH_4 conversion, whereas the 3W one presented in a slight form the typical Pd/PdO hysteresis phenomenon close to 650°C.

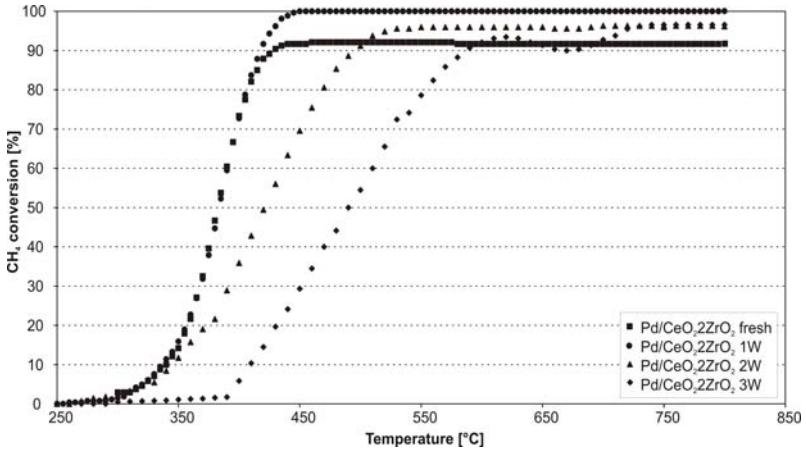

Fig. 3 CH_4 conversion vs temperature for 2% $Pd/CeO_2{\cdot}2ZrO_2$ in fresh and aged status.

The BET values, reported in Tab. 1 together with the mean grain size calculated via the Scherrer equation [13], were very high (strongly related to the synthesis method that allows to process powder with high surface area [1]) and showed a slight worsening with ageing, and sintering effect, according also with FESEM analysis: 74.6, 65.3, 34.8 and 21.5 m^2/g from the fresh to the 3W sample, respectively; the higher the surface area value the better the catalytic activity towards CH_4 combustion. The obtained O_2 TPD curves are drawn in Fig. 4: for the fresh, 1W and 2W aged samples the peaks were "on horseback" of about 600°C. On the contrary, the 3W sample gave a complete oxygen desorption in the range 700-800°C.

Tab. 1 BET, grain size, $T_{10}/T_{50}/T_{90}$ values for 2% $Pd/CeO_2{\cdot}2ZrO_2$ in fresh and aged status.

2% $Pd/CeO_2{\cdot}2ZrO_2$	BET [m^2/g]	Grain size [nm]	T_{10} [°C]	T_{50} [°C]	T_{90} [°C]
fresh	74.6	56	335	380	415
1 week	65.3	75	335	380	425
2 weeks	34.8	85	340	420	490
3 weeks	21.5	96	405	490	580

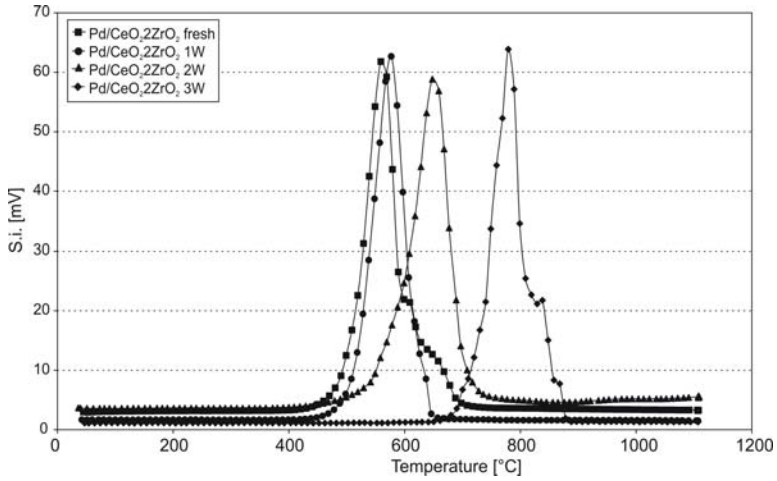

Fig. 4 O_2 TPD curves for 2% $Pd/CeO_2{\cdot}2ZrO_2$ in fresh and aged status.

Tab. 2 reports the total specific moles of desorbed O_2; assuming 600°C as a cut temperature, the specific moles of O_2 desorbed below and above this temperature are also listed, together with the peak temperature (T_p), assumed as an index of the desorption mean temperature. The total specific moles of desorbed O_2 remain practically the same for the fresh and aged samples (average value: 52.18 μmol/g ± 4.2%); moreover, also the shape of the four TPD curves remain nearly the same. Comparing the TPD and TPC tests results, it appears a tight link between the O_2 desorption temperature and the catalytic activity: the lower the O_2 desorption temperature range (see the T_p values), the higher the catalytic activity toward CH_4 combustion. The trend of T_{90} (combustion TPC) and T_p (O_2 desorption TPD) are, in fact, in close agreement.

Tab. 2 O_2 TPD results for 2% Pd/CeO_2·2ZrO_2 in fresh and aged status.

2% Pd/CeO_2·2ZrO_2	total O_2 [μmol/g]	O_2 below 600°C [μmol/g]	O_2 above 600°C [μmol/g]	T_p [°C]
fresh	54.25	46.10	8.15	535
1 week	49.86	39.88	9.98	550
2 weeks	52.72	10.55	42.17	650
3 weeks	51.89	-	51.89	790

3.2. FT-IR studies

Figure 5A shows the FT-IR spectra of surface species detectable on fresh and aged catalyst powders, following outgassing at 500°C. Carbonate species, evident on the fresh catalyst, are characterized by broad and strong peaks at 1540 and 1420 cm^{-1} (CO_3 asymmetric stretchings). Over similar mixed Ce-Zr system, carbonate formation has been related mainly to the presence of exposed Ce ions. Molecular CO_2 inclusion is revealed by the sharp peak at 2340 cm^{-1}. The weak band at 2120 cm^{-1} is a peculiar feature assigned to the electronic transition of Ce^{3+} ions in internal structural defects [14] suggesting that in these experimental conditions some reduced Ce ions exist, not limited to the surface. Ageing at 900°C for 1W, 2W and 3W leads to the detection of both surface and bulk sulphates, the latter prevailing over the 2W and 3W aged catalysts. In particular, new sharp components at 1360 and 1270 cm^{-1} appear already follwing 1W ageing and can be assigned to S=O stretching mode of surface sulfate species. The complex and strong absorption centred around 1000-950 cm^{-1}, with pronounced shoulder around 1070 and 990 cm^{-1}, is due to S-O stretching modes of more ionic sulfates [15]. Carbonate species could still be detected in the spectrum of the 1W aged catalyst, but completely disappear in 2W and 3W sample spectra. This behaviour provides evidence for a competition between CO_2 and SO_2 on the basic surface sites. The band at 2120 cm^{-1} disappeared in the 2W/3W samples spectra, suggesting that the catalyst was fully oxidized.
Low temperature CO adsorption over the fresh sample (figure 5B) allows the detection of Pd in several oxidation states: Pd metal clusters strongly interacting with the surface, forming terminal carbonyls characterized by stretching band at 2100 cm^{-1}($Pd^{0/\delta+}$-CO); larger metal particles, forming terminal carbonyls characterized by bands at lower frequency (Pd^0-CO); and Pd ions, whose carbonyl stretching band above 2100 cm^{-1} superimposes with the band due to CO adsorbed over Ce ions [16]. Pd clusters increased their dimensions following 1W ageing (see a weak band due to CO bridging species ($Pd^0{}_2CO$)) but after 2W and 3W ageing all the IR signals are strongly reduced in intensity and Pd metal particles appear to be no more available to CO coordination. Poisoning is likely due to surface/bulk sulphate formation, which hinders accessibility to metal surface species.

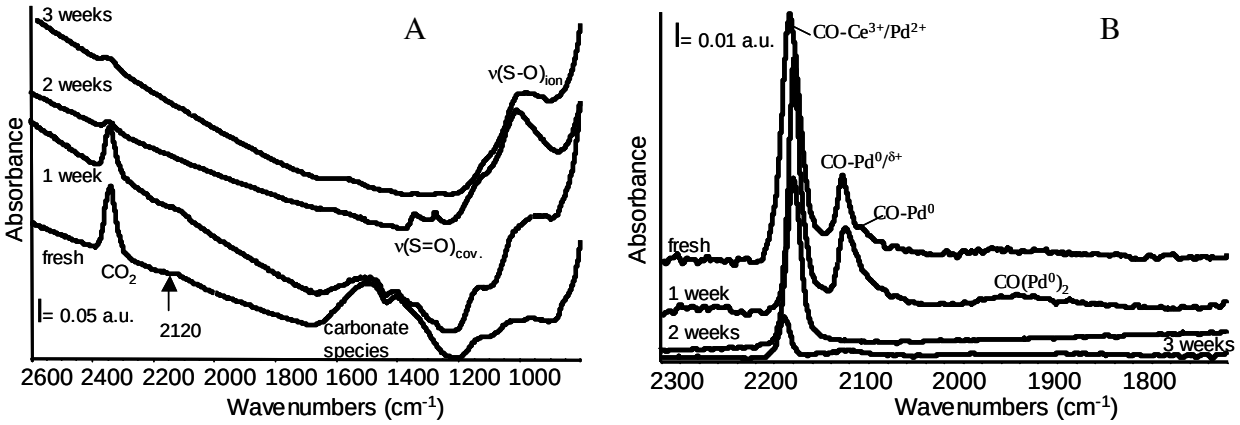

Fig. 5. (A) FT-IR spectra of 2% Pd/CeO_2·2ZrO_2 in fresh and aged status. Pure powders outgassed at 500°C. (B) FT-IR spectra of surface species arising from CO adsorption over outgassed 2% Pd/CeO_2·2ZrO_2 in fresh and aged status. Liquid nitrogen temperature.

4. Conclusions

Pd/CeO_2·2ZrO_2 catalyst for NG combustion was developed and characterized after increasing thermal ageing and S-compounds poisoning treatment. Prevailing ageing mechanisms seem Pd metallic clusters coalescence detected over the Ce-Zr system, and surface-bulk sulfates formation, the latter destroying the initial crystallographic structure. Prolonged tests with radiant premixed catalytic burners lined with the developed catalyst are under investigation to verify the performance of the developed catalytic material also in the structured form.

5. References

1. Zwinkels M.F.M., S.G. Järås S.G.et al.: *Catal. Rev. Sci. Eng.*, **35**:319 (1993).
2. Specchia S., Ahumada Irribarra M.A. et al.: *Ind. Eng. Chem. Res.*, **46**:6666 (2007).
3. Müller C.A., Maciejewski M. et al.: *J. Catal.*, **166**:36 (1997).
4. Boaro M., Vicario M. et al.: *Catal. Today*, **77**:407 (2003).
5. Pisarello M.L., Milt V. et al.: *Catal. Today*, **75**:465 (2002).
6. Sekar M.M.A., Manoharan S.S. et al.: *J. Mater. Sci. Letters*, **9**:1205 (1990).
7. Patil K.C., Aruna S.T. et al.: *Curr. Op. Solid State Mater. Sci.*, **2**:158 (1997).
8. Specchia S., Civera A. et al.: *Catal Today*, **117**:427 (2006).
9. Zhang-Steenwinkel Y., Castricum H.L. et al.: *J. Catal.*, **221**:523 (2004).
10. Rosso I., Garrone E. et al.: *Appl. Catal. B: Env.*, **30**:61 (2001).
11. Klvana D., Delval J. Et al.: *Appl. Catal. A: Gen.*, **165**:171 (1997).
12. Civera A., Negro G. et al.: *Catal. Today*, **100**:275 (2005).
13. Interrante L.V., Hampden-Smith M.J.: *Chemistry of Advanced Materials.* Wiley N.Y. (1998);
14. Finocchio E., Daturi M., et al.: *Catal. Today* **52**:53 (1999).
15. Waqif M., Basin P., et al.: *Appl. Catal. B: Environ.*, **11**:193 (1997).
16. Hadjiivanov K.I., Vayssilov G.N.: *Adv. Catal.*, **47**: 308 (2002).