

## Ageing mechanisms on PdO<sub>x</sub>-based catalysts for natural gas combustion in premixed burners

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### ABSTRACT

The ageing effect induced by S-compounds over 2%Pd/CeO<sub>2</sub> · 2ZrO<sub>2</sub>, 2%Pd/LaMnO<sub>3</sub> · 2ZrO<sub>2</sub> and 2%Pd/BaCeO<sub>3</sub> · 2ZrO<sub>2</sub> catalysts for CH<sub>4</sub> combustion was investigated; S-compounds are in fact added as odorants in the natural gas network for safety purposes. Pd-based catalysts were prepared by solution combustion synthesis (SCS), starting from metal nitrates/glycine mixtures. Basic characterization (XRD, BET, FESEM analysis), FT-IR studies and catalytic activity tests were performed on powders and after accelerated ageing carried out up to 2 weeks (hydro-thermal treatment at 900 °C under a flow rate with typical domestic boiler exhaust gas composition, 9% CO<sub>2</sub>, 18% H<sub>2</sub>O, 2% O<sub>2</sub> in N<sub>2</sub>, containing also 200 ppmv of SO<sub>2</sub> to emphasize any poisoning effect). Over fresh catalysts, IR analysis of CO adsorption evidenced the formation of highly dispersed Pd metal clusters and Pd ions. With ageing, 2%Pd/CeO<sub>2</sub> · 2ZrO<sub>2</sub> increased its CH<sub>4</sub> combustion half-conversion temperature (*T*<sub>50</sub>, regarded as an index of catalytic activity) from 382 °C—recorded for fresh sample—to 421 °C, attained with the same sample aged two weeks. An unexpected improvement was found instead in the overall performance of 2%Pd/LaMnO<sub>3</sub> · 2ZrO<sub>2</sub> and 2%Pd/BaCeO<sub>3</sub> · 2ZrO<sub>2</sub>: the *T*<sub>50</sub> in fact lowered from 570 to 450 °C for the first one, and from 512 to 443 °C for the second one, after two weeks ageing. S-hydro-thermal treatment provoked bulk and surface sulfates formation on all aged samples, with a concentration increasing with the exposure time. Prevailing ageing mechanisms seemed to be Pd metallic clusters coalescence, detected over the Ce–Zr system, and surface-bulk sulfates formation, the latter destroying the initial crystallographic structure. In 2%Pd/LaMnO<sub>3</sub> · ZrO<sub>2</sub> and 2%Pd/BaCeO<sub>3</sub> · ZrO<sub>2</sub> powders the amount of the perovskite phase strongly decreased during ageing, in favor of the formation of bulk sulfate and of oxides.

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### 1. Introduction

In accordance with the last climate policy (e.g. Kyoto protocol), reduction of HCs/CO/NO<sub>x</sub>/CO<sub>2</sub> emissions and increase of safety and efficiency in the natural gas (NG) combustion processes have recently become even more important since its demand as energy source has been increasing worldwide. In the recent years, catalytic combustors for gas turbines and domestic appliances evolved from research level to field-testing and commercial scale, claiming lower NO<sub>x</sub>, CO and unburned HC emissions than any equivalent device relying on conventional combustion (Forzatti and Groppi, 1999). To increase the performance, in terms of overall efficiency and control of pollutant emissions, the adoption of catalysts to better control the NG oxidation could help in going towards the limits imposed by the Kyoto protocol.

PdO<sub>x</sub>-based ZrO<sub>2</sub>-stabilized catalysts were chosen, in line with earlier investigations (Specchia et al., 2004, 2006, 2007), thanks to their very good performance; an attempt was made to exploit ageing/poisoning mechanism at powdered level. PdO<sub>x</sub>-based catalysts in fact, are well-known as excellent catalysts towards NG oxidation (Forzatti and Groppi, 1999). ZrO<sub>2</sub> acts as structural promoter, in that its presence limits the specific surface area loss caused by prolonged exposure to high temperatures (Müller et al., 1997). In particular, the mixed oxide system of CeO<sub>2</sub>–ZrO<sub>2</sub> is a very promising catalyst: CeO<sub>2</sub> is appreciated as promoter for many employments in catalytic combustion with noticeable application as automotive exhausts oxidation catalyst (Palmisano et al., 2006). CeO<sub>2</sub> in fact, shows a good capability of changing rapidly its oxidation number from Ce<sup>3+</sup> to Ce<sup>4+</sup> state, with a consequent O<sub>2</sub> fast release from its lattice to the nearby species (Pisarello et al., 2002; Boaro et al., 2003). The simultaneous synthesis of a perovskite phase such as LaMnO<sub>3</sub> and of a suitable second oxide with good thermal resistance (e.g. ZrO<sub>2</sub>) that can act as a structural promoter, was investigated and found beneficial in terms of both higher specific surface area and better

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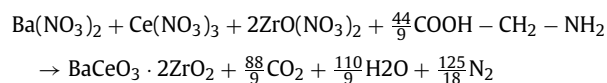
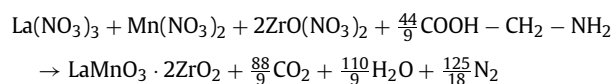
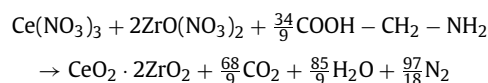
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resistance to high temperatures (Specchia et al., 2006). The last proposed catalyst is a mixed oxides system based on the BaCeO<sub>3</sub> perovskite co-synthesized with ZrO<sub>2</sub>. The BaO–CeO<sub>2</sub> system oxide is actually studied as storage–oxidation–reduction catalyst (Lotta et al., 2002; Boaro et al., 2003).

The solution combustion synthesis (SCS) preparation route, used to synthesize an impressive variety of fine particle oxides and adopted in the present work to prepare PdO<sub>x</sub>-based ZrO<sub>2</sub>-supported catalysts, represents an interesting alternative to common techniques for its potential advantages: relatively cheap starting reactants; simple and easily available organic molecules as fuel; highly exothermic and self-sustaining reactions.

## 2. Experimental

2%Pd/CeO<sub>2</sub> · 2ZrO<sub>2</sub>, 2%Pd/LaMnO<sub>3</sub> · 2ZrO<sub>2</sub>, and 2%Pd/BaCeO<sub>3</sub> · 2ZrO<sub>2</sub> powdered catalysts were prepared via SCS, a process based on the oxidation of an organic fuel, like glycine, which provides the necessary synthesis heat (Zwinkels et al., 1993). Metal nitrates of Ce, La, Mn, Ba, and ZrO (Aldrich, 99% purity), were used as precursors, acting as oxidizers of glycine in solution. The organic molecule plays a double role: by forming complexes with metal cations in aqueous solution, it guarantees good solution homogeneity, preventing the preferential precipitation of ionic species; moreover, it reacts with the precursors (metal nitrates). The overall combustion reactions can be written as follows:



The prepared aqueous solutions were transferred in a ceramic dish and placed into an oven pre-heated at 450 °C. After water evaporation, the heat released in the fast reaction allowed the formation of the catalytic powders. Subsequently, the as-prepared powders were calcined in oven at 800 °C for 2 h in still air (Specchia et al., 2007), so as to favor decomposition of the eventually unreacted nitrate precursor. A 2% by weight of Pd was added in a stoichiometric amount by adding Pd(NO<sub>3</sub>)<sub>2</sub> in the initial aqueous solution.

Since Pd/oxide-based catalysts are prone to be poisoned by sulfur compounds (used as odorants in natural gas networks), the catalytic powders were kept in an electric tubular oven at 800 °C under a flow rate with typical domestic boiler exhaust composition (9% CO<sub>2</sub>, 18% H<sub>2</sub>O, 2% O<sub>2</sub> in N<sub>2</sub>); 200 ppmv of SO<sub>2</sub> were added too. The latter value was chosen several times higher than the odorant supplementary concentration in commercial NG (about 8 ppmv, in Italy, as tetrahydrothiophene, THT) so as to accelerate any possible poisoning effect (Specchia et al., 2004, 2006, 2009). Earlier sulfur poisoning studies on perovskite catalysts showed that the basic poisoning mechanism under catalytic combustion conditions was chemisorption of SO<sub>2</sub>/SO<sub>3</sub> species generated by combustion of whatever sulfur-organic compound present in the feed (Specchia et al., 2007). The catalytic powders were continuously aged up to 2 weeks.

The fresh and 1/2 weeks (1W/2W) aged samples of all the as-prepared catalysts were characterized by X-ray diffraction (XRD, Philips PW1710 equipped with a monochromator for the Cu K $\alpha$  radiation), BET measurements (Micromeritics ASAP 2010 M) and Scanning Electron Microscopy (SEM, FESEM Leo 50/50 VP with Gemini column). Catalytic activity towards CH<sub>4</sub> oxidation was then evaluated in a lab-scale plant: 0.1 g of catalyst powder mixed with 0.9 g of

SiO<sub>2</sub> were inserted in a quartz tube (4 mm I.D.), sandwiched between two quartz wool layers. The fixed-bed microreactor thus obtained fed with 50 N cm<sup>3</sup> min<sup>-1</sup> of a gaseous mixture containing CH<sub>4</sub> (2%), O<sub>2</sub> (16%) and He (balance), was placed into a PID regulated electrical oven. Starting from 800 °C, the temperature—measured by a thermocouple placed alongside the quartz tube—was decreased and the outlet CO<sub>2</sub>, CO, CH<sub>4</sub> and O<sub>2</sub> concentrations were determined by a continuous analyzer (NDIR and paramagnetic URAS 14, ABB), thus allowing to calculate CH<sub>4</sub> conversion and estimate the half-conversion temperature (T<sub>50</sub>) of each catalysts.

Finally, pure fresh and aged catalyst powders were pressed in self supporting disks and treated in vacuum in IR cell connected to gas manipulation apparatus. All samples were outgassed at 500 °C and cooled at liquid N<sub>2</sub> temperature before CO adsorption. Spectra were recorded in the temperature range—130 °C—room temperature by a Nicolet Nexus FT instrument. Catalyst powders were diluted in KBr in order to record skeletal spectra.

## 3. Results and discussion

Table 1 summarizes BET data and mean grain size (calculated via the Scherrer equation, (Interrante and Hampden-Smith, 1998)) of all fresh and aged catalytic powders: the obtained values were very high (strongly related to the synthesis method that allows to process powder with high surface area, (Zwinkels et al., 1993)), in particular for the 2%Pd/LaMnO<sub>3</sub> · 2ZrO<sub>2</sub> in the fresh status. All the catalysts showed a BET area worsening with ageing, together with sintering effect, according also with FESEM analysis (Fig. 1); an increase of the mean grain size was also detectable. Particularly, the higher the BET values on the fresh samples, the higher the BET value decay with ageing: 2%Pd/LaMnO<sub>3</sub> · 2ZrO<sub>2</sub> catalyst presented the worst BET area decrease.

The FESEM images (Fig. 1) show that for all the catalytic systems, the fresh powders explained a typical microstructure, characterized by a spongy form, perforated waffles with nanometric pores and complex network configuration. After 1 week of treatment, the morphology changed radically exhibiting a notched surface. Sintering phenomena occurred after 2 weeks of ageing: 2W samples in fact, showed a smooth surface with micro porosity in a range of about 1  $\mu$ m. Moreover, Pd clusters with dimensions less than 100 nm were

**Table 1**

BET specific surface area, grain size and T<sub>10</sub>/T<sub>50</sub>/T<sub>90</sub> of fresh and aged (1 week: 1W; 2 weeks: 2W) PdO<sub>x</sub>-based catalysts.

	BET (m <sup>2</sup> g <sup>-1</sup> )	Grain size (nm)	T <sub>10</sub> (°C)	T <sub>50</sub> (°C)	T <sub>90</sub> (°C)
<b>2%Pd/CeO<sub>2</sub> · 2ZrO<sub>2</sub></b>					
F	74.6	56 <sup>a</sup> ; 11 <sup>b</sup>	340	382	429
1W	65.8	75 <sup>a</sup> ; 10 <sup>b</sup>	336	383	419
2W	34.8	85 <sup>a</sup> ; 12 <sup>b</sup>	345	421	498
<b>2%Pd/LaMnO<sub>3</sub> · 2ZrO<sub>2</sub></b>					
F	132.5	45 <sup>c</sup> ; 10 <sup>b</sup>	450	570	645
1W	69.8	88 <sup>c</sup> ; 9 <sup>b</sup>	500	625	690
2W	21.6	–	360	450	550
<b>2%Pd/BaCeO<sub>3</sub> · 2ZrO<sub>2</sub></b>					
F	26.4	78 <sup>d</sup> ; 54 <sup>e</sup>	414	512	592
1W	22.7	–	540	628	694
2W	15.4	–	330	443	540

<sup>a</sup>Referred to CeO<sub>2</sub>;

<sup>b</sup>Referred to ZrO<sub>2</sub>;

<sup>c</sup>Referred to LaMnO<sub>3</sub>;

<sup>d</sup>Referred to Ce<sub>2</sub>Zr<sub>3</sub>O<sub>10</sub>;

<sup>e</sup>Referred to BaZrO<sub>3</sub>.

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