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Role of Pd loading and dispersion on redox behaviour and CH_4 combustion activity of Al_2O_3 supported catalysts

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ABSTRACT

In this work the effect of palladium load (1–4%, w/w) and particle size (2–6 nm) on the catalytic activity in CH_4 combustion and on the reduction/reformation behaviour of PdO during alternate CH_4-reducing/CH_4-lean combustion pulses was investigated over Al_2O_3 supported catalysts. PdO-reduction/reformation cycles occurring during the tests were confirmed to be beneficial with respect to deactivation phenomena observed during prolonged exposure to lean combustion atmosphere. The results showed that the catalyst with lower Pd load and higher metal dispersion exhibits a lower specific catalytic activity in CH_4 combustion, which is likely associated with a lower reducibility of smaller PdO particles as evidenced by CH_4-TPR experiments. The more dispersed system also showed a slower reactivation dynamics upon exposure to lean combustion atmosphere. Such behaviour has been tentatively associated with the presence of ultradispersed species that during oxidation form poorly active aluminate complexes first, which are then slowly transformed into reducible PdO.

1. Introduction

The use of natural gas fuelled vehicles (NGVs) is developing very rapidly in most industrial countries for economical, political and environmental reasons. The use of natural gas in the automotive sector represents a promising alternative to gasoline and diesel because it allows energy source diversification. Besides, it is attractive also for environmental reasons since the emissions of several pollutants (NO_X, SO_X, particulate matter) can be maintained at very low limit values to preserve health and environment [1]. Focusing on emissions of greenhouse gases, natural gas is characterized by high H/C ratio which allows to reduce tailpipe CO_2 emissions, at given combustion engine efficiency. Besides NGVs can be operated in lean conditions, this permits a more efficient combustion, compared to stoichiometric operations, and reduces NO_X emissions thanks to lower combustion temperatures associated with the high air to fuel ratios (typically 20 or greater).

Nevertheless, the "green" image of lean burn NGVs risks to be compromised by emissions of unburned CH_4 which is a strong greenhouse gas, with a global warming potential more than one order of magnitude higher than that of CO_2. Catalytic combustion represents a promising option to match with severe limitations on CH_4 emissions [1]. In the reaction conditions specific of exhausts (low temperature, 300–400 °C; presence of 10–15% of water vapour; large excess of O_2; low CH_4 concentrations, 500–1000 ppm) Pd supported catalysts are widely recognised as the most active in CH_4 combustion [1–4]. Consequently, several studies have been undertaken to identify the factors which influence the activity of palladium supported catalysts, such as the state of oxidation of Pd, the reactivity of the different forms of PdO_X and the particle size of palladium aggregates.

Several literature reports have established the importance of PdO for methane combustion [5–10] and many studies have been dedicated to the understanding of which is the optimum state of PdO_X between chemisorbed oxygen, a PdO skin on a Pd metal core or bulk PdO [1]; most of these studies has indicated the two latter forms as the most active state of Pd supported catalysts [5–15].

The effect of Pd particle size on catalytic activity is an issue still debated in literature: while most of the research groups have reported that methane combustion is a structure sensitive reaction, there have been some contradictory suggestions [16].

In a previous investigation [17] it was shown that alternate reduction/re-oxidation cycles under CH_4 containing atmosphere performed over Al_2O_3 supported Pd catalysts provide benefit both on deactivation phenomena, which occurs during prolonged

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operation under lean CH_4 combustion conditions, and on regeneration of S-poisoned Pd catalysts. Along these lines in this work the effect of Pd load and dispersion on catalytic activity in methane combustion and on redox behaviour of palladium supported on alumina catalysts was investigated in the presence of alternate reduction/re-oxidation cycles under CH_4 containing atmosphere. Attention was focused on correlation between the catalytic activity and Pd oxidation process in order to understand how Pd particle size influences both these phenomena and their correlation. Alternated reduction/re-oxidation cycles were performed in the presence of H_2O since it is well known from the literature that H_2O markedly influences the activity of Pd catalysts in CH_4 combustion by both strong kinetic inhibition [18] and poisoning effect [17,19,20].

2. Experimental

2.1. Catalyst preparation

Palladium catalysts supported on Al_2O_3 (Sasol® Puralox SBA 140) were obtained by incipient wetness impregnation using an aqueous solution of $Pd(NO_3)_2$ (Alfa Aesar®, density 1.427 g/ml, 14.67%, w/w). The support was calcined in air at 950 °C for 10 h (specific surface area 100 m^2/g, pore volume 0.49 cm^3/g, θ-Al_2O_3 phase with the presence of γ-Al_2O_3 in traces). Catalysts with different Pd loading were prepared (1%, 2% and 4% (w/w)) by single step impregnation. The catalysts were dried at 110 °C and finally calcined in air at 600 °C for 10 h.

2.2. Catalyst characterization

The experimental Pd loading was determined by atomic absorption method on a Varian AA110 apparatus. XRD patterns were recorded on a Philips (PW 1050/70) powder diffractometer using a vertical goniometry and the Cu Kα radiation ($\lambda_{K\alpha}$ = 0.1518 nm). Specific surface areas were measured by liquid nitrogen adsorption at 77 K using a Micromeritics Tristar apparatus according to the Brunauer–Emmett–Teller (BET) method.

The Pd particle size and morphology were studied by Transmission Electron Microscopy (TEM) using a Philips CM120 instrument at different magnification (200 nm, 100 nm and 20 nm scale).

H_2 chemisorption experiments for the measurement of palladium dispersion were carried out on a Micromeritics AutoChemII instrument; the catalysts were reduced in 50 Ncc/min of 5% H_2 in Ar at 500 °C for 1 h; after a 2 h purge with 50 Ncc/min of Ar, the temperature was decreased. 5% H_2 in Ar pulses (0.961 ml loop) were injected at regular interval times at 70 °C. A H/Pd = 1/1 stoichiometry was assumed for H_2 adsorption on metallic palladium. The mean Pd particle diameters d_P (nm) were estimated from dispersion data using the following expression derived from hemispherical particles [21]:

$$d_P = \frac{6C_a PM \times 10^9}{\rho D N_{av}}$$

with C_a concentration of surface metal atoms, equal to 1.27×10^{19} atoms/m^2 [22], PM Pd atomic mass, ρ Pd volumetric mass equal to 12.02×10^6 g/m^3 [22], D metal dispersion and N_{av} Avogadro number.

In situ Raman measurements were carried out on an Horiba Jobin Yvon HR800UV LabRam spectrometer using green light laser (514 nm). The experimental procedure is described as following: (i) the sample was pre-treated under 1% O_2/N_2 at 600 °C for 1 h. After cooling down to 30 °C under the same atmosphere, Raman spectra was recorded; (ii) after purge under N_2, reducing atmosphere was introduced, 2% CH_4/N_2; (iii) heating step at 10 °C/min was stopped at different temperature values for 10 min in order to record Raman spectra under N_2. For each spectrum acquisition, CH_4 was removed from the feed because its presence modified the signal intensity.

In situ X-ray diffraction experiments were carried out on a Bruker AXS D8 advance powder diffractometer using the Cu Kα radiation ($\lambda_{K\alpha}$ = 0.15186 nm). Patterns were recorded for 2θ values comprised between 25 and 85° by 0.030° step, with dwell time of 0.2 s (equivalent to 6 min 40 s of acquisition by diffractogram). The 2-theta values used in order to identify PdO and Pd^0 peaks are 35, 40, 54 and 59° and 39, 46 and 82°, respectively. The cell support for in situ XRD measurements was made of Kanthal with the main diffraction peaks at 44.48, 64.78 and 82.28° (relative intensity: 100/20/50) with the following dimensions: deep < 1 mm, width = 10 mm, length = 20 mm. The experimental procedure was the same as described for Raman analysis. However, CH_4 was kept in the feed during XRD data acquisition.

2.3. Alternated lean combustion/reducing pulses and CH_4-TPR tests

The performances of 1%, 2% and 4% Pd/Al_2O_3 catalysts were studied using a fixed bed tubular quartz microreactor (I.D. = 7 mm) at atmospheric pressure, placed within an electrically heated furnace. Catalytic bed consisted of 60 mg of catalytic powder (74–105 μm), diluted by 60 mg of quartz for the 1% and 2% Pd/Al_2O_3 samples and by 180 mg of quartz for the 4% Pd/Al_2O_3 one. Temperature were monitored by a K-type thermocouple located in the middle of the catalytic bed. Reactants and products compositions at the outlet of the reactor were monitored by a mass spectrometer with quadrupole detector (Balzers QMS 422) and were periodically verified through a HP6890 GC system.

Alternated lean combustion/CH_4-reducing pulses were performed over 1%, 2% and 4% Pd/Al_2O_3 catalysts at constant temperature values (325 °C, 350 °C and 375 °C), according to the following procedure: the catalyst were operated for 30 min under lean combustion conditions (0.5% CH_4, 4% O_2, 1% H_2O, 2% N_2, He at balance, 150 cm^3/min at STP, GHSV = 150 000 Ncm^3/(g h)) at constant temperature; then a 30–40 s purge (He + 5% N_2) was performed to allow the desorption of species adsorbed on catalytic surface and to purge the dead volumes. After the purge, the feed was switched to a reducing stream (0.5% CH_4, 1% H_2O, He at balance, 150 cm^3/min at STP, GHSV = 150 000 Ncm^3/(g h)), at the same temperature. After another purge, the lean combustion conditions were finally restored. Argon was always feed with CH_4 and used as tracer to separate the two different atmospheres and to clearly identify the actual switch between the lean or CH_4-reducing atmosphere and the purge.

Temperature programmed reduction under methane containing atmosphere (CH_4-TPR) was carried out in the following conditions: 0.5% CH_4, 1% H_2O, He at balance, 150 cm^3/min at STP, GHSV = 150 000 Ncm^3/(g h); the temperature was ramped up to 500 °C and down to room temperature at 15 °C/min.

3. Results

3.1. Characterization

The results of characterization analyses performed on the three samples are summarized in Table 1. In all the cases, the actual Pd loadings, obtained by atomic absorption analyses were close to the nominal ones. Specific surface area (SSA) was about to 100 m^2/g for all the three fresh catalysts indicating that there was no significant effect of the Pd loading on the SSA which is determined by the thermal treatment of the alumina support.

Hydrogen chemisorption experiments indicated that the three samples exhibit different dispersion of palladium on alumina; in

Table 1
Main characteristics of conditioned 1%, 2% and 4% (w/w) Pd/Al_2O_3 catalysts.

Theoretical Pd loading (%)	AAS Pd loading (%)	BET SSA (m^2/g)	H_2-chemisorption dispersion (%)	Pd particle size (nm)		
				H_2-chemisorption	TEM	XRD
1	1.01	106.2	48	2	<8	Not det.
2	2.14	106.3	21	5	>8	7
4	3.94	104.4	19	5	>8	6

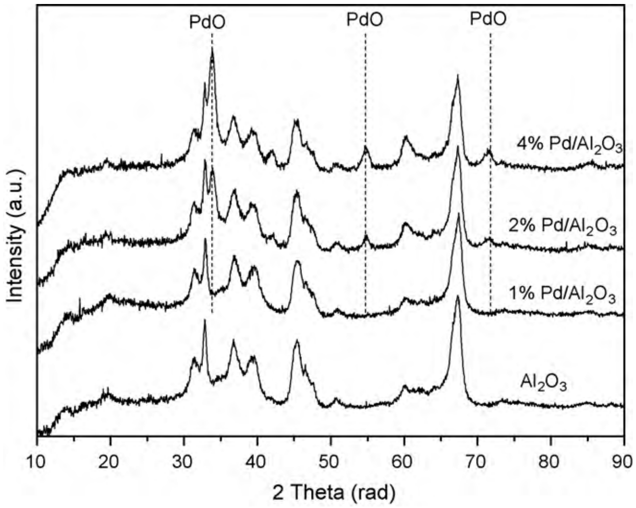

Fig. 1. XRD patterns for the fresh 1%, 2% and 4% (w/w) Pd/Al_2O_3 and for the support.

particular the 1% Pd catalyst was characterized by a higher dispersion value (48%) than the 2% and 4% samples, which were equally dispersed (21% and 19%, respectively). The size of Pd particles estimated from dispersion data is about 2 nm for the 1% Pd samples and about 5–6 nm for both the 2% and 4% ones.

XRD spectra are shown in Fig. 1 in comparison with XRD patterns of the alumina support. The XRD analysis indicated the presence of only PdO phase while no metallic Pd was detected. In the spectrum of 1% Pd sample neither PdO nor Pd peaks were detected due to low metal loading and high dispersion of palladium particles. Crystallite size estimated on the basis of the width at half-height of PdO peaks is about 7 nm and 6 nm, respectively, for the 2% and for the 4% Pd samples, in good agreement with results of H_2 chemisorption experiments. This implies that reduction of PdO under H_2 at 500 °C does not promote further agglomeration/growth of Pd particles.

TEM pictures for the 1%, 2% and 4% Pd catalysts are shown in Fig. 2. Although it was not possible to define a statistics of Pd particle size distribution because of the low contrast between palladium and alumina, some qualitative observations can be done. All the samples present homogeneous distribution of PdO on the support and are characterized by palladium particle dimensions of few nm, as indicated by XRD and H_2 chemisorption analysis. Also TEM pictures evidence that 1% Pd catalyst is more dispersed than the 2% and 4% ones which are similarly dispersed, with particle size lower then 8 nm and larger then 10 nm, respectively. The increasing trend of palladium dispersion with metal loading indicated by TEM analysis is in agreement with literature indications [23].

3.2. Catalytic activity

The three investigated catalysts were conditioned by means of repeated Pd oxidation/reduction cycles, performed alternating lean combustion conditions and short CH_4-reducing pulses at 350 °C, since this procedure has been found effective in achieving a stable catalytic behaviour, as reported in a previous work [17].

Fig. 3 shows the time evolution of CH_4 conversion in a sequence of lean reaction conditions alternated to CH_4-reducing pulses at 350 °C for the stabilized 1%, 2% and 4% Pd/Al_2O_3 catalysts. For all the investigated systems CH_4 conversion during lean combustion conditions showed a trend characterized by a sharp increase followed by a moderate gradual deactivation resulting in the presence of a maximum; the activity lost during the prolonged exposure to the lean combustion atmosphere is completely recovered after a subsequent CH_4-reducing pulse followed by re-oxidation under lean combustion conditions. This behaviour was reproducible in many Pd oxidation/reduction cycles after the initial stabilization.

The final catalytic activity of the 1%, 2% and 4% Pd/Al_2O_3 catalysts is compared in Fig. 4, in terms of time evolution of CH_4 conversion at different temperatures (325 °C, 350 °C and 375 °C). Comparison of activity levels indicates that the more dispersed catalyst (1% Pd/Al_2O_3) is less active than the less dispersed ones (2%

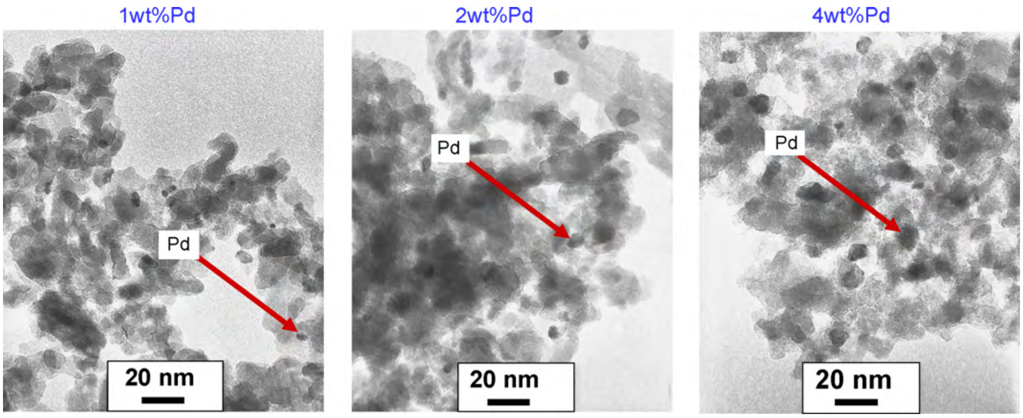

Fig. 2. TEM pictures for the 1%, 2% and 4% Pd/Al_2O_3 catalysts.

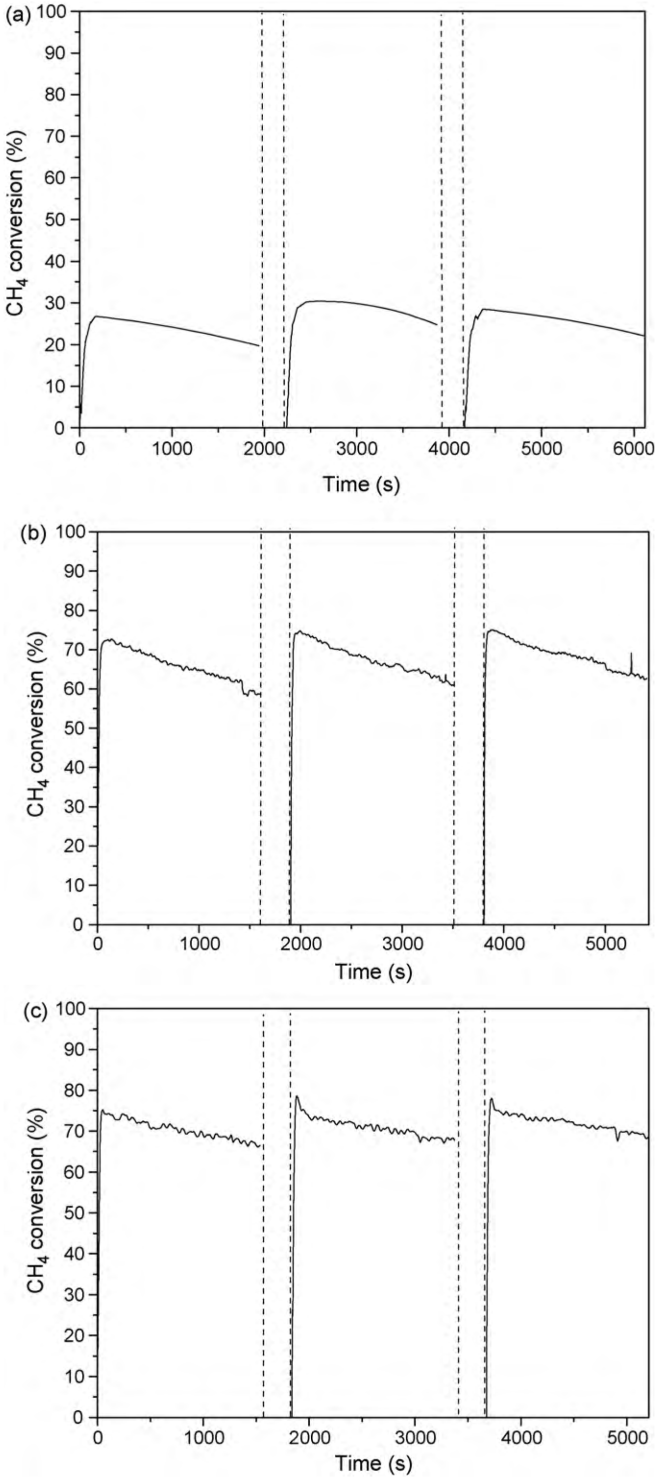

Fig. 3. Time evolution of CH_4 conversion in a sequence of alternate lean combustion/CH_4-reducing pulses experiment at 350 °C on stabilized 1% Pd/Al_2O_3 (a), 2% Pd/Al_2O_3 (b) and 4% Pd/Al_2O_3 (c) catalysts. Intervals between vertical dotted lines corresponds to CH_4-reducing pulses.

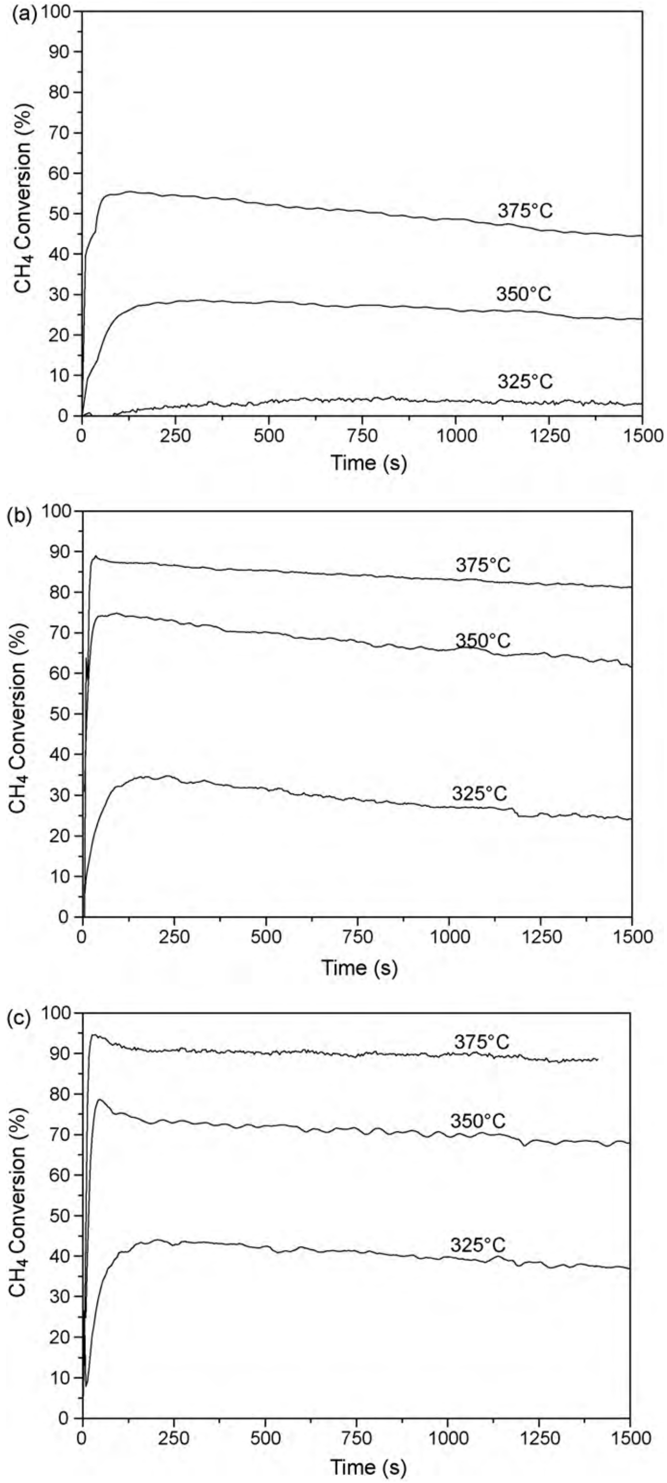

Fig. 4. Time evolution of CH_4 conversion of 1% (a), 2% (b) and 4% (c) Pd catalysts at 325 °C, 350 °C and 375 °C.

Pd/Al_2O_3 and 4% Pd/Al_2O_3). For example, after 10 min of lean combustion at 350 °C the 1% Pd/Al_2O_3 catalyst provided a CH_4 conversion of 25% while the 2% and 4% Pd/Al_2O_3 ones showed 65% and 70% conversions, respectively.

Turnover frequencies (TOFs) for the three samples were estimated on the basis of CH_4 conversion data at 350 °C after 10 min under lean conditions, assuming a plug flow behaviour of the reactor and a first order dependent on CH_4 and −1 order dependent on H_2O kinetic, in line with previous studies [24–27]. TOFs were then re-evaluated at following conditions: $P_{CH_4} = 0.5$ kPa, $P_{H_2O} = 1.1$ kPa, $T = 350$ °C. The number of catalytic active sites estimated by H_2 chemisorption pulses analysis were used for this purpose. This technique allows determining the number of available metallic palladium sites, whereas there is a general agreement in the literature [5,8,9,15,23] that active sites associated with CH_4 combustion are likely PdO sites, although

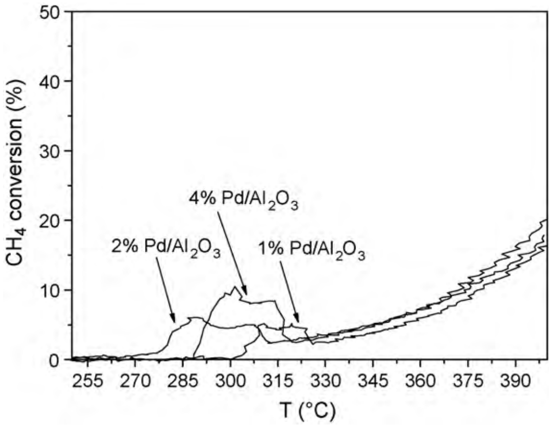

Fig. 5. Temperature evolution of CH_4 conversion during TPR for conditioned 1%, 2% and 4% Pd/Al_2O_3 catalysts.

there is not consensus on their exact nature. However TOF literature values are commonly referred to the number of metallic palladium active sites, with few exceptions [28], so that the method we adopted can be useful for the sake of comparison.

For the 1%, 2% and 4% Pd/Al_2O_3 catalysts by TOF values of $0.071\,s^{-1}$, $0.37\,s^{-1}$ and $0.27\,s^{-1}$ were calculated, respectively. Notice that the more dispersed sample has a turnover frequency about 4–5 times lower than the two catalysts with higher Pd loading, which exhibit similar dispersions and TOFs. The values herein estimated were compared with those reported in the literature [6,21,26,28–32] re-evaluated at the following conditions: $P_{CH_4} = 0.5\,kPa$, $P_{H_2O} = 1.1\,kPa$, $T = 350\,°C$, assuming 1, −1 and 0 reaction order dependence on CH_4, H_2O and O_2 and an activation energy of 120 kJ/mol. The TOFs reported for the less dispersed 2% Pd and 4% Pd catalysts, are comparable to those reported by Ribeiro and co-workers for Pd foil [28], which are the highest values of TOFs in a wide literature range from $0.001\,s^{-1}$ [31] to $0.397\,s^{-1}$ [28].

Activation energies for the investigated catalytic systems were estimated on the basis of data shown in Fig. 4. CH_4 conversion data after 10 min under lean conditions were used. Values of 136 kJ/mol, 118 kJ/mol and 122 kJ/mol were calculated for 1%, 2% and 4% Pd catalyst, respectively, which compares well with those reported in the literature estimated taking into account water inhibition effect on CH_4 combustion kinetic [28–30].

3.3. PdO-reduction

Reducibility of the 1%, 2% and 4% Pd/Al_2O_3 catalysts was studied by means of CH_4-TPR [32]; the results are shown in Fig. 5. In all the cases it was observed an initial CH_4 conversion peak, in correspondence of which only CO_2 and H_2O were detected. A further gradual increase of CH_4 conversion was then observed, associated with H_2 and CO release.

Literature indications suggest that the reduction of PdO to metallic Pd involves some structural complexities [33], however, independently to the reaction mechanism, the amount of CH_4 consumption and CO_2 release observed during the TPR initial peak were in agreement with the following stoichiometry:

$$4PdO + CH_4 \rightarrow 4Pd^0 + CO_2 + 2H_2O \tag{1}$$

Once Pd metal formed, steam reforming and water gas shift reactions started and were responsible for CH_4 consumption and H_2 and CO production at higher temperature. Reduction of PdO for fresh 2% and 4% Pd samples started at 275 °C and 285 °C, respectively, and finished at 315 °C and 320 °C while for 1% Pd catalyst PdO-reduction occurred at higher temperatures, beginning at 300 °C and finishing at 325 °C.

The PdO-reduction temperature ranges were also investigated by means of in situ Raman analysis. In Raman spectra presented in Fig. 6, the peak located at 640 cm^{-1} was associated to PdO, in line with previous literature indications. Mamede et al. [34] have carried out in situ Raman analysis on 1 wt% Pd/γ-Al_2O_3. They found a main peak attributed to PdO but slightly shifted to lower wave numbers, i.e. 626 cm^{-1}. This difference can be attributed to the use of the Nd:YAG laser excitation line at 532 nm, higher than that used in the present study (512 nm). They attributed this Raman line to the Raman active B_{1g} vibration mode of PdO. Bell and co-

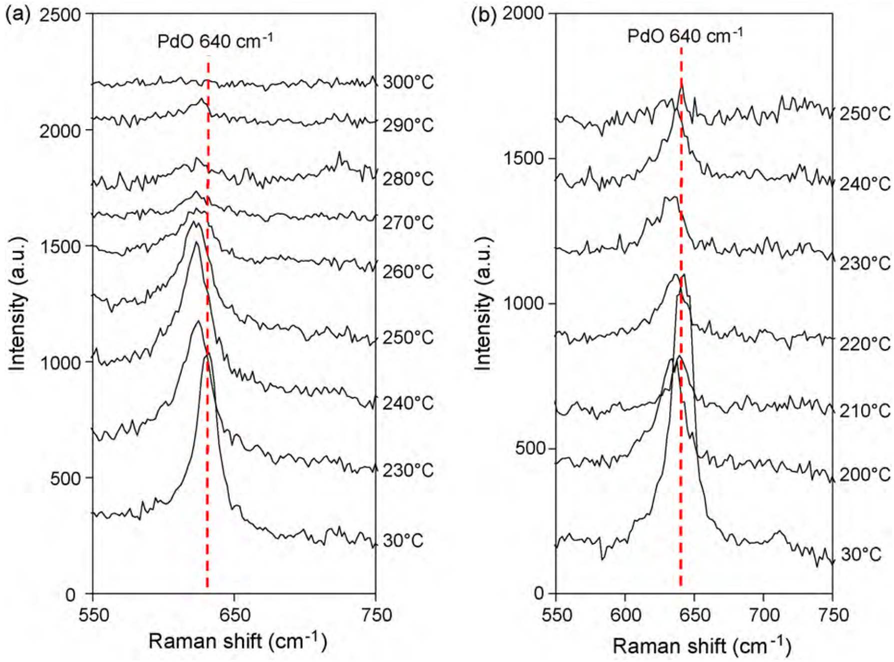

Fig. 6. Raman spectra of (a) 1% and (b) 4% Pd/Al_2O_3 catalysts under CH_4/N_2 at different temperature.

workers [32] found the main PdO peak at 651 cm^{-1} on 10 wt% Pd/ZrO_2 with the 514.5 nm wavelength of the Ar ion laser. Arai et al. [35] found evolution of the main PdO peak between 626 cm^{-1} (40 °C) and 633 cm^{-1} (600 °C) on sputtered PdO_X thin film with the 632.8 nm wavelength of the He–Ne laser.

For the 1% and 4% Pd/Al_2O_3 catalysts studied in this work, temperatures corresponding to the total PdO-reduction (i.e. disappearance of the 640 cm^{-1} band) are 290 °C and 250 °C, respectively (Fig. 6) which qualitatively confirms the reducibility differences observed by CH_4-TPR (Fig. 5). Note that such temperatures are lower than those observed in the CH_4-TPR experiments; this effect is due to the absence of H_2O in the feed of in situ Raman experiments, as confirmed by the results of CH_4-TPR experiments performed with dry feed.

3.4. PdO-oxidation/reactivation

Palladium oxidation and the correlated catalytic activity evolution during the exposure of the three investigated catalysts to lean combustion conditions following CH_4-reducing pulses were investigated at different temperatures.

The catalytic activity trends during the lean combustion phase after a CH_4-reducing pulse at different temperatures (325 °C, 350 °C and 375 °C) are shown in Fig. 4 for the 1%, 2% and 4% Pd/Al_2O_3 samples. As mentioned above at each temperature value, all the samples showed a similar qualitative trend in catalytic activity: upon restoring lean combustion condition, first a fast CH_4 conversion increase was observed, followed by a moderate decrease with time; losses of methane combustion activity observed during prolonged exposure to lean combustion atmosphere were completely recovered after a CH_4-reducing pulse.

System reactivation at 350 °C is completed in about 300 s for the 1% Pd/Al_2O_3, time in correspondence of which CH_4 conversion reaches its maximum value of about 30%, while at the same temperature the 2% and 4% Pd/Al_2O_3 catalysts exhibit a faster reactivation dynamics, with CH_4 conversion taking about 60 s to reach its maximum value (75%).

The alternate lean combustion/CH_4-reducing pulse experiment performed at the temperature of 325 °C and 375 °C on the three investigated catalysts showed qualitative trends of CH_4 conversion during the lean combustion pulse similar to those observed at 350 °C, characterized by a marked increase up to a maximum value, followed by a gradual deactivation. In Fig. 7, the time to reach CH_4 maximum conversion is reported for the three samples as a function of the temperature. As already evidenced for the experiments at 350 °C, also at 325 °C and 375 °C the dynamics of reactivation of 1% Pd/Al_2O_3 is slower than those of 2% and 4% Pd/Al_2O_3, which are quite similar. The experiments at different temperatures also evidenced that the dynamics of reactivation becomes faster on increasing the temperature, for any Pd load of the catalyst.

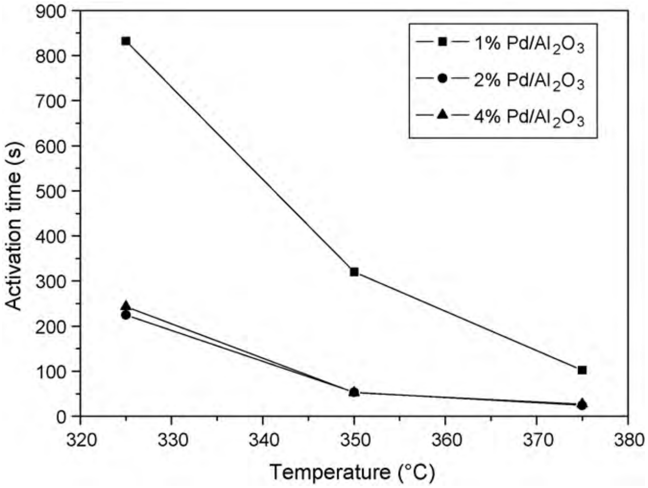

Fig. 7. Activation time during lean combustion reaction following a reducing pulse as a function of the temperature for 1%, 2% and 4% Pd/Al_2O_3.

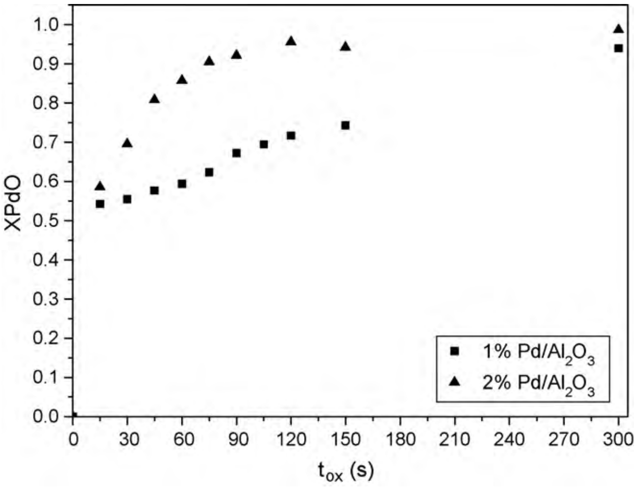

Fig. 8. Extent of metal Pd re-oxidation during lean combustion reaction in function of time lengths of exposure to lean combustion atmosphere at 350 °C, for 1% and 2% Pd/Al_2O_3 catalysts.

The extent of metal Pd re-oxidation during lean combustion reaction was quantified by means of CH_4-TPR experiments performed upon exposure of 1% and 2% Pd/Al_2O_3 catalysts to lean combustion atmosphere at 350 °C for time lengths ranging from 15 s to 30 min.

In these experiments, which were performed only on 1% and 2% Pd catalysts taken as representative of the two different palladium dispersion herein investigated, after a given time under lean combustion atmosphere at 350 °C the catalysts were rapidly quenched down to 200 °C, then CH_4-TPR were performed according to the procedure described in Section 2 to quantify the amount of reducible PdO.

Fig. 8 shows the extent of Pd oxidation as a function of time exposure under lean combustion atmosphere for the two investigated samples. For 2% Pd/Al_2O_3 the extent of palladium oxidation gradually increases with time, being completed in 75–100 s. For 1% Pd/Al_2O_3 catalyst Pd oxidation apparently involves two steps: a fast oxidation up to 55% of total Pd loading, occurring in 15–30 s, followed by a slower step which takes more than 300 s to achieve complete re-oxidation of Pd.

4. Discussion

The results collected in this work confirmed that periodical reducing treatments are beneficial with respect to deactivation occurring during prolonged exposure to lean combustion atmosphere.

Tests performed in a previous work with H_2O-free oxidizing pulses following the reduction treatment [17], indicated that H_2O poisoning is likely responsible for the observed deactivation, in line with many literature indications [2–4,36–38]. The reasons for the water poisoning effect is widely debated in literature and different explanations have been proposed. Some authors [37] associated water poisoning to the slow conversion of the active PdO phase into a less or poorly active $Pd(OH)_2$ phase. Other authors invocated either smoothening of PdO crystallites with decrease of active surface [36] or sintering of palladium particles [3]. However, in line with the results of a previous work [17], our alternated lean combustion/CH_4-reducing pulse experiments evidenced that for all 1%, 2% and 4% Pd/Al_2O_3 catalysts, water poisoning is completely reversible upon reduction/re-oxidation cycles. This behaviour could be associated with decomposition of $Pd(OH)_2$ and/or in roughening of the newly formed PdO surface [36], whereas redispersion after sintering is unlikely.

CH_4 conversion data of the three samples showed that intrinsic combustion activity increases with particle size, i.e. on increasing the Pd load. A 5-fold increase of TOF was evaluated for the 2% (w/w) sample with Pd particle size of 5–6 nm with respect to the 1% (w/w) sample with Pd particle size of about 2 nm. This trend is in line with previous literature reports on Al_2O_3- [21,31] and ZrO_2- [6,26] supported Pd catalysts and correlates well with reducibility of PdO as determined by CH_4-TPR and in situ experiments. This is in agreement with a Mars–van Krevelen redox mechanism for CH_4 combustion over supported Pd catalysts [6–8,39] and suggests that oxygen is more strongly bound to palladium in small particles than in large ones, likely due to interactions with the support.

Dynamics of reactivation upon exposure to lean combustion atmosphere also exhibit peculiar effects associated with Pd dispersion. All the samples initially show a marked increase of activity associated with the re-oxidation of Pd^0 formed during the previous reducing step.

The process is faster on increasing the temperature in line with literature indications reporting activation energy of about 100 kJ/mol for the oxidation of supported Pd particles [12]. On the other hand, despite of oxidation is expected to be faster for smaller particles, the most dispersed 1% Pd sample showed a slower reactivation than the less dispersed 2% and 4% Pd catalysts. Determination of the extent of Pd oxidation by means of CH_4-TPR performed upon exposure of the 1% and 2% Pd catalysts to lean combustion atmosphere at 350 °C for different time lengths showed that for the 2% Pd/Al_2O_3 sample the extent of palladium oxidation gradually increases with time and it is completed in 60–75 s, which is comparable with time required by the reactivation process (50–60 s). On the other hand the 1% Pd sample showed a more complex behaviour: oxidation proceeds through two steps, a fast one up to an extent of oxidation of 50–60% of total Pd, occurring in 15–30 s, followed by an apparently slower oxidation process, taking more than 300 s to achieve complete oxidation of Pd. A similar trend was reported in the literature for large Pd particles supported onto Al_2O_3 and ZrO_2 [12,21] and was associated to the onset of a slower oxidation mechanism governed by oxygen diffusion through the shell of previously formed PdO upon a certain degree of oxidation. Such a mechanism is unlikely to occur in the 1% Pd system herein investigated with average particle size of Pd of 2–3 nm. Alternatively the second slow oxidation step might be ascribed to the presence of ultra dispersed Pd species, strongly interacting with the support. One can speculate that such ultradispersed species can be easily reoxidised but form quite stable aluminate species that are not reducible during CH_4-TPR. Such species would take a longer time under lean combustion atmosphere to be transformed into reducible PdO. The formation of poorly reducible Pd species strongly interacting with the support has been already reported in the literature [40,41] for Al_2O_3 supported systems with low metal loading.

Fig. 9 illustrates the trends of normalized combustion activity (a/a_{max}) versus the extent of Pd oxidation, calculated during the first 300 s of lean combustion pulses at 350 °C, for the 1% and 2% Pd catalysts. In both the samples, the normalized activity has been assumed equal to zero in correspondence with the initial metallic state of Pd. For the 2% Pd system, the activity initially increases slowly reaching only 15% of the maximum value after 15 s when already 60% of oxidation is achieved. Then the activity gradually increases with extent of oxidation up to 1 min (Fig. 9) where the maximum level is reached in correspondence to 85–90% of Pd oxidation extent. Finally activity gradually decreases upon completion of the oxidation process. The 1% Pd catalyst shows a different behaviour: normalized activity weakly increases from 0 to 0.2 after 15 s, when apparently 55% of palladium is oxidized; then the activity shows a sharp increase up to 0.9 without significant variation of the extent of oxidation, followed by a poor increment of normalized activity with the extent of PdO formation.

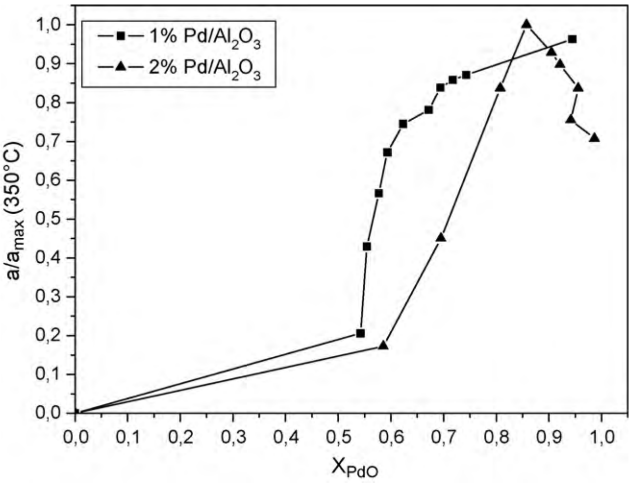

Fig. 9. Normalized catalytic activity during lean combustion reaction at 350 °C as a function of the extent of PdO reformation for 1% and 2% Pd/Al_2O_3 catalysts.

Concerning the correlation of catalytic activity to the extent of Pd oxidation is a widely debated in the literature whether partial or complete oxidation of Pd is required to achieve the maximum activity of CH_4 combustion. Oh et al. [14] indicated a thin layer of PdO on metallic Pd as the active form of the catalyst, while both bulk PdO and oxygen chemisorbed have been claimed to be inactive. Burch and Urbano [8] found that metallic Pd and Pd covered by 1 ML of oxygen are inactive and that catalytic activity of Pd/Al_2O_3 catalysts increases till 3–4 MLs of PdO form on metallic Pd particle; whereas deeper oxidation to bulk PdO does not determine further increase in activity. Also Bell and co-workers [5] found that fully reduced Pd is inactive and that the activity increases with extent of oxidation at 533 K, until a plateau is achieved when 6–7 MLs of PdO form over the surface of Pd crystallites. Some authors also claim that a mixed PdO/Pd phase is a more active state than bulk PdO [33]. This could be alternatively ascribed either to a direct role of metal Pd sites in assisting CH_4 dissociative adsorption or to a promoting effect of Pd in increasing oxygen vacancies of PdO which were proposed as the active sites by Iglesia and co-workers [30]. Along these lines the periodical regeneration associated with alternated reduction/oxidation treatment observed in this work could be ascribed to the reformation of the PdO/Pd mixed state. However it is worth stressing that assuming a shell and core oxidation model for the small particle size of the catalysts herein investigated 6–7 MLs correspond to 85–90% fraction of PdO, which cannot be reliably discriminated from the case of complete oxidation. Besides in addition to the increase of the oxidation degree exceeding an optimum level, other factors, such as smoothening of PdO particles or progressive formation of $Pd(OH)_2$ species associated with prolonged exposure to H_2O containing atmosphere, can also be responsible of the activity decrease in the final part of the oxidation process.

In the case of the 1% Pd sample apparently reactivation proceed up to complete re-oxidation of palladium. However it is worth noting that the increase of the oxidation from 70% to 95% of the total Pd amount only results in a 10% increment of combustion activity. This suggest that the ultradispersed species obtained forming during the last stage of the PdO reformation process are

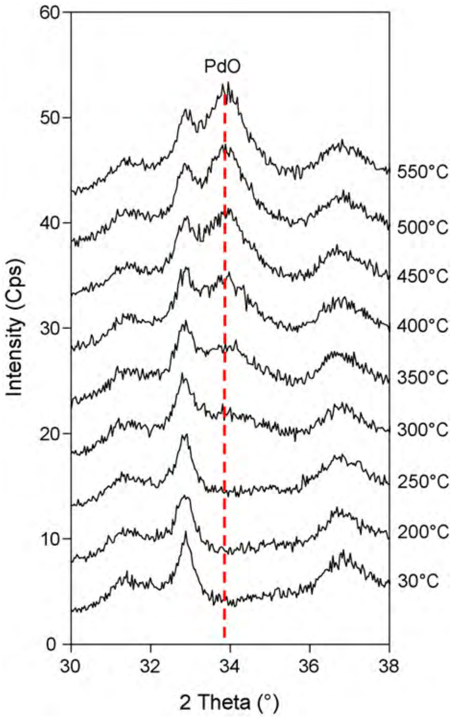

Fig. 10. In situ XRD spectra of 4% Pd/Al_2O_3 catalyst under 20% O_2/N_2 at different temperature after reduction under 2% CH_4/N_2.

poorly active in the combustion of CH_4 and only moderately contribute to the overall activity of the system.

Fig. 9 also shows that marked deviations between the apparent extent of PdO formation and reactivation occur at the early stage of the oxidation process when quite low activity levels correspond to a fraction of PdO higher than 50%. It is likely that at such short exposure period (15–30 s) to lean combustion atmosphere additional time is needed to allow restructuration of the oxide into the active PdO form. This is quite evident in the 1% Pd sample where in the 15–75 s interval of oxidation time a 4-fold activity enhancement is observed in correspondence to very small variations of the apparent fraction of PdO. In this respect note that the procedure herein adopted allowed to evaluate the amount of O_2 uptake occurring upon different oxidation times, whereas no direct spectroscopic evidences were collected on PdO formation during lean combustion pulses. Indeed the time needed for Raman and in situ XRD analysis was too long compared to reactivation time. However, for the 4% Pd/Al_2O_3 catalyst, in situ XRD analysis shows that the formation of PdO crystallites starts at 300 °C (Fig. 10). The PdO crystallisation is very slow and proceeds gradually up to 550 °C.

5. Conclusion

The results of the investigation herein performed on 1%, 2% and 4% (w/w) Pd/Al_2O_3 catalysts pointed out the following main conclusions:

(1) Repeated Pd oxidation/reduction cycles are beneficial to Pd/Al_2O_3 catalysts allowing the complete recovery of the catalytic activity lost during prolonged exposure under lean combustion conditions, possibly associated with H_2O poisoning effects.
(2) The more dispersed catalyst (1% Pd/Al_2O_3) is characterized by a specific CH_4 combustion activity lower than that of the less dispersed ones (2% and 4% Pd/Al_2O_3). In line with previous literature indications such an increase of TOF with particle size is related to the lower reducibility of 'small' than 'large' PdO particles, as evidenced by CH_4-TPR and in situ Raman experiments.
(3) Upon restoring lean conditions after a reducing pulse, reactivation of 1%, 2% and 4% Pd catalysts is associated with re-oxidation of metallic Pd. Reactivation is slower for the more dispersed system (1% Pd/Al_2O_3). For this catalyst formation of PdO apparently involves two steps, the first is likely associated with fast re-oxidation of relatively small Pd particles while the second possibly involves ultradispersed Pd species that rapidly form poorly reducible Pd aluminate which are subsequently slowly transformed into active PdO. On the other hand for the 2% and 4% Pd catalysts reactivation and PdO reformation both occur gradually with comparable time scales. These results suggest a role of a mixed PdO/Pd phase in temporarily enhancing CH_4 combustion activity, but it is worth stressing that due to the relatively small Pd particle size of the systems herein investigated no definite conclusions can be drawn from our data on the issue if either complete or partial re-oxidation of Pd is required to achieve maximum CH_4 combustion activity.
(4) As a whole, the results summarized above confirmed that Pd oxidation/reduction cycles, for example performed through operating strategies based on periodical feeding via a by-pass line of short CH_4 pulses directly to the NGV mufflers [17], might have potential benefic effects on CH_4-emission abatement performances. In this respect the use of highly dispersed Pd catalysts seems to be not advantageous because they are less active compared to less dispersed systems and because their reactivation during lean combustion phase following a CH_4-reducing pulse is slower.

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