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ORIGINAL PAPER

PdO_x/Pd at Work in a Model Three-Way Catalyst for Methane Abatement Monitored by Operando XANES

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Abstract The oxidation state of palladium in a model Pd/ACZ three-way catalyst was monitored by synchronous XANES and mass spectrometry during two consecutive heating (to 850 °C) and cooling (to 100 °C) cycles under stoichiometric conditions simulating exhaust after treatment of a natural gas engine. During heating in the first cycle, PdO reduction occurred around 500 °C and the initial fully oxidized state of Pd was never recovered upon heating and cooling cycles. A mixed Pd^{2+}/Pd oxidation state was at work in the second cycle. Hence, the operando XANES study reveals that the PdO_x/Pd pair exists in a working catalyst but is less active than the catalyst in its initial state of fully oxidized palladium. It is also evident from XANES spectra that ceria–zirconia promotes re-oxidation of metallic Pd, thus reasonably sustaining catalytic activity after exposure to high temperatures.

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1 Introduction

Catalytic methane oxidation holds a pivotal role in energy production [1] and pollution control [2]. Exhaust after treatment technologies of natural gas passenger cars equipped with engines working at stoichiometric air-to-fuel ratios require catalytic control of methane (the major component of natural gas) because of its large global warming potential. Present solutions are based on three-way catalysts (TWC), whose composition is typically very complex given the severe conditions of temperature and of fast transients experienced during operation [3, 4]. Besides Platinum group metals (PGM) that are required to simultaneously reduce and oxidize the major engine exhaust pollutants (CO, NO_x and hydrocarbons), Al_2O_3 is a major component of TWC and offers the required surface area for PGM dispersion and thermal stability. This is further improved by addition of ceria–zirconia (CZ), which also provides the catalyst with the necessary oxygen storage capacity (OSC) required to buffer the fuel rich periods of the catalyst operation [5].

TWC for natural gas fuelled engines are usually enriched with Pd due to its ability to oxidize CH_4 in a wide temperature range and in general the catalytic performance is related to the oxidation state of Pd [6]. Although the nature of the active Pd species is still under debate, a general consensus tends to indicate the necessity for the presence of oxidized Pd (PdO_x) [6–10]. The effect of the addition of ceria is to stabilize PdO [11] thus avoiding large activity losses after exposure to high temperatures, especially under oscillating red-ox conditions. Additionally, there is also indication that the complex chemistry involved in the operation of TWC maybe different between natural gas and gasoline engines and other reactions (than CH_4 oxidation) alone can contribute to CH_4 removal from the exhaust [12, 13]. Therefore, it is of interest to investigate CH_4 oxidation over Pd-based catalysts under simulated exhaust of stoichiometric natural gas engines [12–18].

In this work, a model Pd-only three-way catalyst has been subjected to two consecutive activity cycles under stoichiometric conditions ($\lambda = 1$) in the temperature range of 100–850 °C and the state of Pd was monitored simultaneously by operando XANES/MS.

2 Experimental

The powder alumina and alumina–ceria–zirconia supported Pd samples (hereafter Pd/A and Pd/ACZ, respectively) with 1.6 wt% Pd were kindly provided by Umicore. In situ X-ray absorption near edge structure (XANES) spectra were recorded in the transmission mode at the Pd K-edge ($E_0 = 24.35$ keV) at the beamline X1 of Hasylab (DESY, Hamburg). The electrically heated quartz reactor ($d_i = 20$ mm) was connected to a gas-feeding system with mass-flow controllers and was interfaced to a mass spectrometer [7]. The sample (400 mg, sieved 150–200 μm) was firmly placed between two plugs of quartz wool, one end being placed against a quartz frit. The reactor was mounted in the furnace so that the X-ray beam passed axially through the reactor tube and the optical pathlength coincided with the catalyst bed length (ca. 2 mm). After pre-treatment at 500 °C for 30 min in 21 vol.% O_2/He (400 ml/min), the oxidation state of Pd was monitored by XANES during two heating–cooling cycles in the temperature range of 100–850 °C (5 °C/min) under dry stoichiometric conditions of natural gas engines ($\lambda = 1$, 7,000 ppm CO, 1,300 ppm CH_4, 1,600 ppm NO, 5,300 ppm O_2, bal. He, GHSV = 76,000/h). The reactor outlet was connected to a mass spectrometer (Omnistar, Pfeiffer) to analyze gaseous products by following the m/z values of 2 (H_2), 4 (He), 15 (CH_4), 18 (H_2O), 22 (N_2O and CO_2), 28 (CO), 30 (NO) and 44 (CO_2). The raw XANES data were analyzed using the IFEFFIT software package [19].

3 Results and Discussion

CH_4 oxidation on Pd-based catalysts in the wide temperature range up to 850 °C is characterized by (i) the typical activity drop between 700 and 500 °C and (ii) hysteresis loops during the cooling segment under the reactants feedstock. Figure 1 shows that such characteristics are maintained under stoichiometric conditions (CH_4, CO, NO_x and O_2) of CH_4 oxidation on the model Pd/ACZ three-way catalyst (TWC). The MS signals of the pollutants are provided in Figure S1. During heating in the reactants, light-off of CH_4 abatement of Pd/ACZ occurs at ca. 300 °C and complete conversion is attained at ca. 500 °C. After heating to 850 °C, the cooling segment exhibits a severe activity drop (by 46 %) between 700 and 500 °C with minimum at 587 °C followed by a partial gain of activity with conversion maximum of 85 % at 475 °C, which is typically attributed to Pd re-oxidation [6]. The CH_4 activity drop is accompanied by increased NO emissions (Fig. S1). In the second heating–cooling cycle, the heating segment shifts to higher temperature. Light-off occurs at slightly higher temperature (+20 °C) and only 97 % conversion is obtained at 500 °C (cfr. inset of Figure S1), whereas complete conversion is observed only above 750 °C. The cooling segment well reproduces the profile of the first heating–cooling cycle, except for a slightly larger activity loss (48 %) at higher temperature (ca. 590 °C) and for an apparent improved activity below 350 °C.

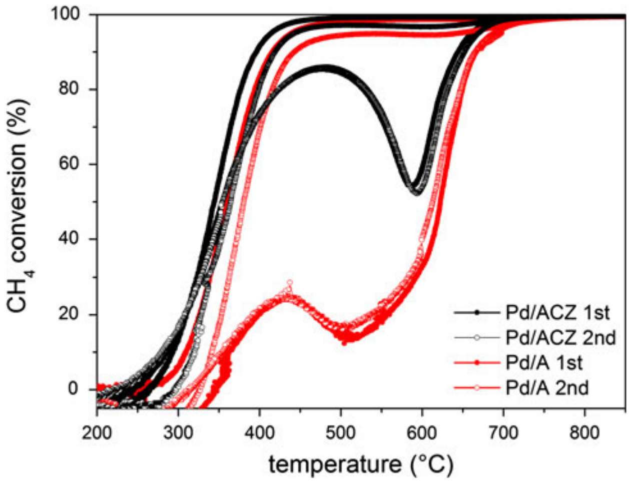

Fig. 1 CH_4 conversion profiles for Pd/ACZ and Pd/A under simulated stoichiometric conditions of natural gas engines during two heating–cooling cycles

Although the present data cannot be conclusive on the chemistry involved in the simultaneous abatement of CO, NO and CH_4 because of the absence of other major components of the engine exhaust (H_2O, CO_2, H_2), some characteristics should be mentioned. NO concentration decreases substantially between 170 and 260 °C in both heating–cooling cycles simultaneously to CO oxidation. This could be due to the CO + NO reaction or the simultaneous CO oxidation and NO reduction on different sites [12]. Heating–cooling segments exert some influence on CO and NO abatement efficiencies. The conversion profile of NO is as temperature dependent as that of CH_4. In the case of CO, though conversion is complete at 200 °C the apparent increase of CO concentration between 370 and

850 °C reveals that either CH_4 reforming or reverse water gas shift is possibly at work above 370 °C. Both NO reduction by CH_4 and CH_4 (steam) reforming have been mentioned as possible concurrent reactions to CH_4 oxidation responsible for CH_4 removal from the exhaust [12]. The present data confirm that direct CH_4 oxidation is not the only reaction contributing to this process under dry stoichiometric conditions.

For the sake of comparison, Pd/A demonstrates slightly higher light-off temperature (+10 °C) than Pd/ACZ but the heating segment otherwise parallels that of Pd/ACZ. An activity plateau is attained at 98 % CH_4 conversion at 600 °C and full conversion is obtained only at 850 °C. In the cooling segment, the activity drop reaches 86 % at ca. 500 °C and only a poor activity gain is observed up to a conversion of ca. 25 % at 430 °C before activity vanishes. The second cycle exhibits similar features to that of Pd/ACZ. However, the initial activity gain reaches only 95 % CH_4 conversion at 540 °C, followed by a subtle activity loss at around 600 °C before full conversion is obtained at 850 °C. Also in the case of Pd/A, the cooling segment is very similar to the heating one.

Figure 1 shows that under stoichiometric conditions Pd/ACZ is systematically superior to Pd/A with respect to both low temperature CH_4 oxidation activity and re-oxidation of Pd after exposure to 850 °C under the reactants feedstock.

The activity profile of Fig. 1 can be rationalized by analyzing the oxidation state of Pd during reaction using operando XANES. At room temperature the two catalysts Pd/ACZ and Pd/A exhibit the typical whiteline of the Pd K-edge of supported PdO (Figs. 2 and S2). The XANES spectra have been evaluated by linear combination analysis (LCA) using the spectra of PdO for Pd^{2+} and of the Pd foil for metallic Pd. Given these two reference spectra, the LCA of Fig. 3 provides only an immediate visualization of the variation of the oxidation state of Pd during the activity profiles of Fig. 1 that well describes the changes in the XANES spectra of Figs. 2, S2 and S3. During heating Pd/ACZ under stoichiometric conditions, Pd reduction is observed to occur already around 500 °C, which is remarkably lower compared to lean conditions (>750 °C) [7]. The intervention of reducing conditions favoring CH_4 reforming above 370 °C caused by the lower oxygen concentration at complete CO oxidation is the likely driving force. The onset of reduction corresponds to the observed increase of CO concentration (Figure S1).

In the cooling segment, a continuous re-oxidation of metallic Pd is observed in the whole temperature range. However, after the full cycle, the original state of Pd was not restored (Fig. 2). Therefore, contrary to the first cycle a mixed PdO_x/Pd state is at work in the second cycle between 200 and 500 °C. Further reduction occurs again above 400 °C while heating, whereas the partial re-oxidation

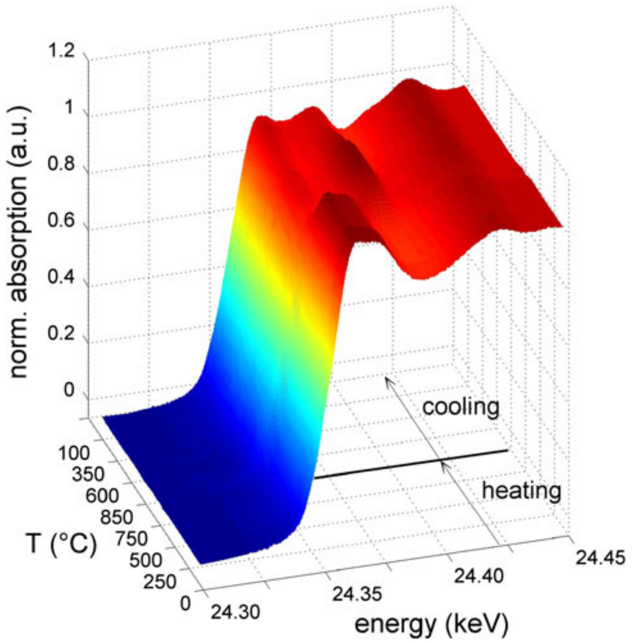

Fig. 2 Operando XANES spectra at the Pd K-edge recorded during the first heating–cooling cycle for Pd/ACZ. The spectra were collected simultaneously to the activity profile of Fig. 1

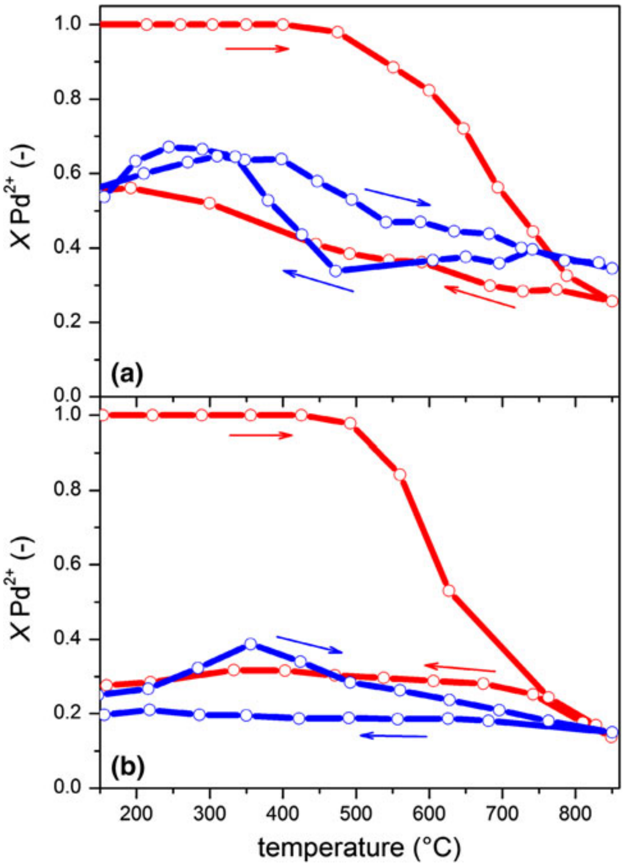

Fig. 3 Variation of the fraction of Pd^{2+} determined by LCA for **a** Pd/ACZ and **b** Pd/A for the activity profiles of Fig. 1

presents a maximum below 400 °C in the cooling segment. Despite the approximation of the LCA, the final state after the second cycle coincides with that obtained after the first cycle. Therefore, the catalyst persists in the mixed PdO_x/Pd state.

The most substantial difference with Pd/A is that on Pd/A Pd re-oxidation in the cooling segment occurs to a much lesser extent in both cycles and the oxidation state of Pd systematically exhibits lower levels of Pd^{2+} species than on Pd/ACZ (Fig. 3).

The observed difference of low temperature activity between the heating segments of the first and second cycles may be associated with the different oxidation state of Pd, oxidized Pd in the fresh sample and the mixed PdO_x/Pd pair after the first cycle. Therefore, we consider that oxidized Pd is required for activity at low temperature, below 400 °C [7]. However, even if high temperature is not attained fully oxidized Pd is not a realistic state in a working three-way catalyst as indicated by the onset of reduction under these conditions at 400 °C (the average reaction temperature for the real TWC). Though appearing slightly less efficient than fully oxidized Pd, the PdO_x/Pd pair is the realistic active phase during reaction. Its structure cannot be disclosed out of this set of data. A major question is related to the possible local co-existence of PdO_x and metallic Pd or to the preferential distribution of the two phases on alumina and ceria zirconia [11]. Possibly, the nature of PdO_x/Pd pair is also associated with larger particles than on the fresh catalyst as a result of the high temperature exposure [7, 20].

Finally, it appears that the presence of oxidized Pd is crucial also in the temperature regime where Pd re-oxidation takes place (400–600 °C) in the cooling segment. This is corroborated by the following observations: (i) the activity gain after the drop in the cooling segment is larger for Pd/ACZ than for Pd/A (Fig. 1) and (ii) the fraction of PdO is larger on Pd/ACZ than on Pd/A in this temperature range (Fig. 3). In contrast to lean burn conditions [7, 21], Pd re-oxidation is incomplete both on Pd/ACZ and Pd/A because of the stoichiometric reaction conditions. However, even under these conditions, Pd re-oxidation is more facile on Pd/ACZ than on Pd/A due to its OSC, signifying the importance of the support contribution to the reaction.

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