Insight into the structure of supported palladium catalysts during the total oxidation of methane†

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The combination of *in situ* X-ray absorption spectroscopy, X-ray diffraction and on-line catalytic data provided insight into the structure–performance relationship of a flame-made Pd/ZrO_2 catalyst during the total oxidation of methane: upon heating, a sudden reduction accompanied by sintering of the Pd-particles, leads to a significantly lower catalytic activity and a hysteresis during cooling down.

Supported palladium particles are presently regarded as the most active catalysts in the total combustion of methane under lean burn conditions.[1–5] They are applied in exhaust catalytic converter systems as well as in catalytic gas turbine combustors. Among the different supported catalysts, Pd/Al_2O_3 and Pd/ZrO_2 have received most attention. We have recently found that Pd-based catalysts prepared by flame-spray pyrolysis exhibit a high catalytic activity.[6,7] However, the mechanism for methane oxidation is complex and there is still an ongoing discussion on the active species.[3] In particular, a characteristic hysteresis in reaction rate is observed during heating and subsequent cooling in a methane–oxygen reaction mixture.[1,3,8]

Depending on the oxygen partial pressure, temperature, size and morphology of the Pd particles or the support, palladium can be present in metallic or oxidic form. Much effort has been undertaken over the past years to unravel the role of metallic and oxidic Pd-species in the reaction. From thermoanalytical studies it was concluded that the Pd-catalysts release oxygen at high temperatures, which is supposed to lead to a deactivation of the Pd-catalysts.[1] Carstens *et al.*[9] further concluded from Raman spectroscopy and TPR that amorphous PdO is more difficult to reduce than crystalline palladium oxide. Moreover, transmission electron microscopy studies revealed tremendous restructuring and thus morphological changes.[10] Recently, kinetic studies have been performed on Pd and PdO films showing that the reaction rates are higher on PdO.[11,12] These studies, like the thermoanalytical results, indicate that PdO is the active species. Nevertheless it has also been reported that a catalyst reduced *in situ* before the methane oxidation reaction is more active than a completely oxidized catalyst.[13,14] Also Lyubovsky and Pfefferle[15] concluded that metallic Pd could be more active for the methane oxidation reaction, especially at higher temperatures. Schalow *et al.*[16] further demonstrated that the oxidation mechanism is particle size-dependent.

This shows that further studies, particularly under reaction conditions, are required. Despite the fact that several *in situ* spectroscopic studies have been reported during methane combustion using Raman spectroscopy,[17] DRIFTS[18,19] and X-ray absorption spectroscopy,[20] none of the studies have been performed at temperatures where deactivation occurs (750–900 °C) on technical catalysts under realistic reaction conditions, which requires appropriate techniques and setups. Moreover, the catalytic performance and the structure should be measured simultaneously[21–24] using complementary techniques.[25–30] This approach allows derivation of structure–catalytic performance relationships.[21–23,27]

Here we present results on an *in situ* study combining both X-ray absorption spectroscopy and XRD with catalytic activity on the Pd-based catalysts. The structure and catalytic activity of palladium-based catalysts were monitored up to 900 °C, *i.e.* above the temperature where deactivation occurs and a hysteresis is observed during cooling down. We chose in the present case flame-made catalysts because they exhibit high activity and the palladium constituent is highly dispersed and exists mainly in an oxidized state after preparation.[6]

Fig. 1 shows a typical hysteresis cycle during heating (steps 1–4) and cooling down over 10% Pd/ZrO_2 (steps 4–7). As for conventional Pd-based catalysts,[1] the catalytic activity drops above 720 °C (step 2 to 3). A strong hysteresis behaviour is found during cooling to 550 °C (compare the activity in step 2 and step 6), which is due to the higher catalytic activity of the flame-made catalysts and which is more distinct than for conventionally prepared catalysts.[6]

In order to shed more light on the oxidation state of the Pd-particles, a special setup was designed that allows heating of the sample to 900 °C with defined ramps under reaction conditions. This facilitates the correlation of the catalytic activity during the

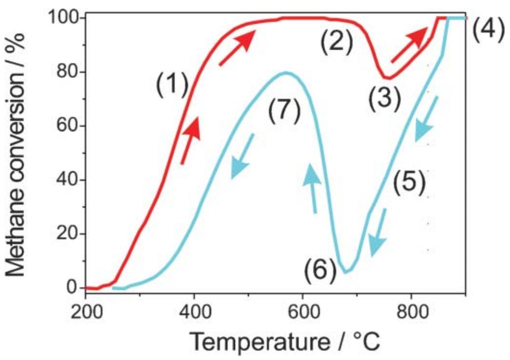

Fig. 1 Hysteresis in methane conversion observed over flame-made 10% Pd/ZrO_2 during temperature-programmed reaction in 1% CH_4–4% O_2 in He; the different steps marked on the lines are referred to in the text.

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heating–cooling cycle with the structure of the catalysts. The setup was based on a microreactor (quartz capillary, similar to the setups in refs. 31 and 32) and a special air blower (up to 1100 °C, Cyberstar S.A., provided by ESRF) serving as an oven for the microreactor. The setup is described in more detail in the ESI.† In addition, both X-ray absorption spectra and X-ray diffraction patterns could be recorded under the same conditions with the same setup on the same sample.

The X-ray absorption spectra, catalytic data and XRD patterns under selected conditions are given in Fig. 2–4. After preparation of the catalysts, the Pd-particles were not visible by XRD (despite a high concentration in the 10% Pd/ZrO_2 catalyst). Therefore during heating most of the structural information was extracted from X-ray absorption spectroscopy. The data show that palladium is mainly in its oxidized state after preparation and can be partially reduced in 5% H_2–He at room temperature (*cf.* Fig. 2 spectra "RT" and "RT, after 5% H_2" (as well as a comparison of EXAFS, XANES and XRD data in the ESI†).

Also after reduction in hydrogen no XRD reflections typical for Pd were observed in the XRD patterns (*cf.* Fig. 4). Such a pre-reduced catalyst was previously reported to be more active in the catalytic combustion of methane.[13,14] During heating in 1% CH_4–4% O_2–He, the palladium is nearly completely re-oxidized, in accordance with previous *in situ* XAS studies.[20] Fig. 2 shows the corresponding XANES spectra during heating to 500 °C, and Fig. 3 the increase of the conversion (similar as in Fig. 1). Note that in the XRD patterns neither PdO nor metallic Pd are discernible (spectrum 2 in Fig. 4). Hence, under these conditions, the palladium constituent was re-oxidized and palladium was well dispersed.

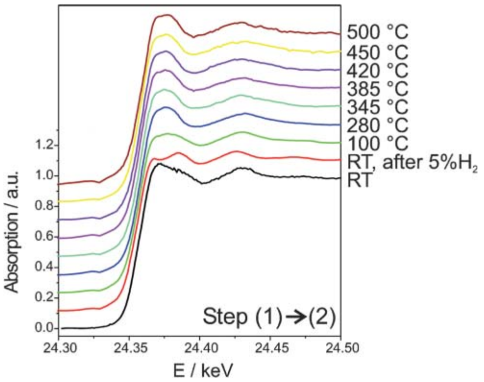

Fig. 2 XANES spectra at the Pd K-edge of as-prepared 10% Pd/ZrO_2, after reduction and during the methane combustion in 1% CH_4–4% O_2–He; in parallel on-line catalytic data (Fig. 3) and XRD data (Fig. 4) were also recorded.

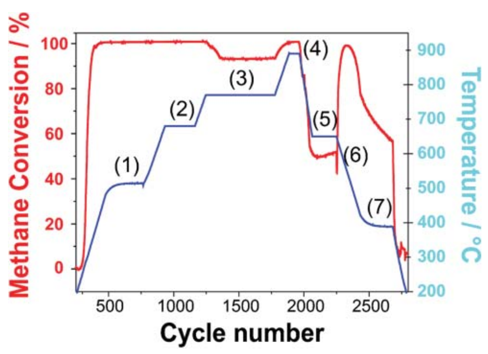

Fig. 3 Methane conversion (red) as function of temperature (blue) during the methane combustion over 10% Pd/ZrO_2 in 1% CH_4–4% O_2/He; the steps correspond to those in Fig. 1.

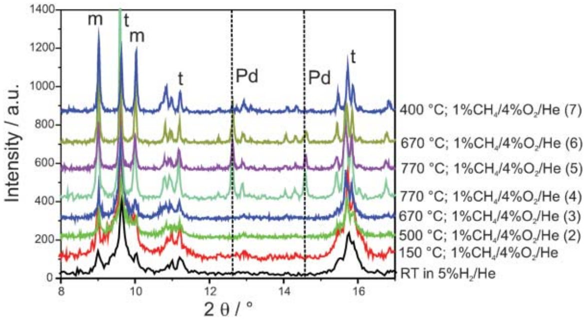

Fig. 4 XRD patterns during methane combustion over 10% Pd/ZrO_2 in 1% CH_4–4% O_2–He; RT: after reduction in 5% H_2–He; (1) 150 °C, (2) 500 °C, (3) 670 °C, (4) 770 °C, (5) after 890 °C down to 770 °C, (6) 630 °C, and (7) 400 °C; "Pd" denotes the position of metallic palladium, "t" tetragonal zirconia and "m" monoclinic zirconia (see ESI† for a zoomed Figure around the characteristic Pd-reflection).

Upon further heating the catalyst to 770 °C (XANES data in Fig. 5), the catalyst first stayed in mainly oxidized state and the methane conversion remained high (*cf.* Fig. 3) but at 740 °C the near edge structure changed (Fig. 5). The whiteline decreased indicating a reduction of palladium. At the same time, metallic palladium appeared in the XRD patterns (Fig. 4, spectrum 4). This implies that metallic palladium forms at high temperatures and, simultaneously, a strong sintering of the palladium particles occurs. Both effects seem to lead to a drop in activity as observed in the on-line catalytic data in Fig. 3 corresponding to the effect observed in step 3 in Fig. 1. According to the XRD patterns, the support is made up of monoclinic and tetragonal zirconia, remaining stable under these conditions.

During further heating to 900 °C, the palladium constituent becomes more reduced and then remains in a metallic state and after a drop in activity like that indicated in Fig. 1, the catalytic

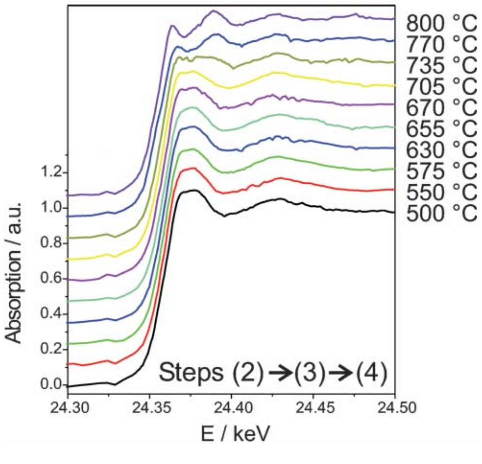

Fig. 5 XANES spectra at the Pd K-edge during methane combustion over 10% Pd/ZrO_2 in 1% CH_4–4% O_2–He; in parallel on-line catalytic data (Fig. 3) and XRD data (Fig. 4) were also recorded.

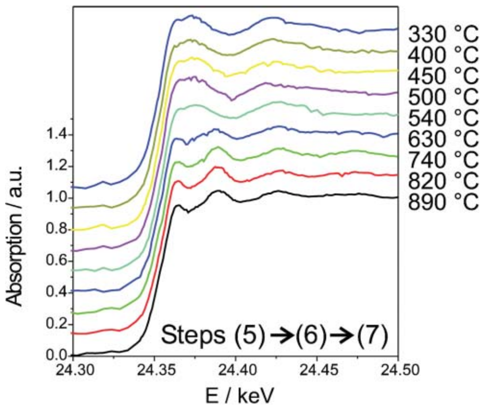

Fig. 6 XANES spectra at the Pd K-edge during methane combustion over 10% Pd/ZrO_2 in 1% CH_4–4% O_2–He (cooling down of the catalyst in the reaction mixture); in parallel on-line catalytic data (Fig. 3) and XRD data (Fig. 4) were also recorded.

activity increases again, probably due to a different oxidation mechanism (gas phase reaction, *cf.* ref. 3).

During cooling, the on-line catalytic data in Fig. 3 evidence a similar hysteresis as shown in Fig. 1 (step 6). The data both from XRD (Fig. 4, spectra 4, 5 and 6) and Pd K-XANES (Fig. 6) reveal that palladium remains in its metallic state. Only at significantly lower temperatures (below 600 °C, step 7), the palladium re-oxidizes and the catalytic activity increases again.

In summary, *operando* XAS and XRD data during the catalytic oxidation of methane were collected. They evidence a direct correlation between the structure and the performance of the catalyst. A strong deactivation is observed during thermal reduction of the catalyst accompanied by sintering of the Pd particles. This supports previous studies by thermal analysis[1] that the reduction of palladium particles leads to a deactivation of the Pd catalysts. Moreover, a strong sintering occurs as demonstrated by the XRD data. Also this leads to a further deactivation of the catalyst. As in other Pd-based catalysts the catalytic activity during a second cycle showed a similar hysteresis as that shown in Fig. 1, and a higher catalytic activity than during the cooling process. This may be traced back not only to a re-oxidation of Pd, evidenced by both EXAFS and XRD, but also a redispersion of the Pd particles as is well-known from other studies on palladium catalysts.[33–35] Note for example, that no PdO reflections can be found in the XRD patterns. However, in the case of the flame-made catalysts, the catalytic activity during the first cycle was much higher than during the second cycle[7] showing that Pd is not completely redispersed. Thus catalysts, that retain palladium in an oxidized and well-dispersed state, like the flame-made catalysts used in this work, are beneficial for total methane oxidation. This stabilization can also be achieved by varying the support material.[3]

To our knowledge, this is the first *in situ* XAS/XRD study at high temperature combined with on-line catalytic data. Like previous studies at lower temperature (*e.g.* in refs. 25, 26 and 28), it demonstrates the potential of parallel XAS (short-range order and geometrical information) and XRD (long range order) analysis under reaction conditions as well as the importance of measuring both the catalytic performance and the structure at the same time for deriving structure–performance relationships. Both the formation of metallic Pd-particles and the associated sintering of Pd seem to lead to the strong deactivation of the catalysts above 770 °C. Due to the rapid re-oxidation of the Pd-particles, these studies need to be performed preferentially above 750 °C to correlate structure and activity.

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