Deactivation aspects of methane oxidation catalysts based on palladium and ZSM-5

Andrey W. Petrov,^{1,2} Davide Ferri,¹ Mohamed Tarik,¹ Oliver Kröcher,^{1,3,*} Jeroen A. van Bokhoven^{1,2,*}

1 – Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland

2 – ETH Zurich, Institute for Chemical and Bioengineering, CH-8093 Zurich, Switzerland

3 – Ecole polytechnique fédérale de Lausanne (EPFL), Institute of Chemical Sciences and Engineering, CH-1015 Lausanne, Switzerland

* Corresponding author

oliver.kroecher@psi.ch

Tel. +41 56 310 2066 Fax +41 56 310 21 99

jeroen.vanbokhoven@chem.ethz.ch

Tel. +41 44 632 55 42 Fax +41 44 632 10 10

Abstract

Catalytic methane oxidation is used in exhaust gas after treatment to reduce methane emissions in stationary combustion processes as well as in natural gas vehicles. Pd/zeolite catalysts provide higher activity than the commonly used Pd/Al₂O₃, but suffer from rapid deactivation under reaction conditions and in the presence of steam. This work presents a detailed study of deactivation of 1 wt.% Pd/H-ZSM-5 catalyst in reaction conditions in dry and wet feed including characterization of both the active phase and the support.

Initially well-dispersed PdO particles are not stable and sinter immediately after the exposure to the reaction mixture even in dry feed and stabilize at lower dispersion level. Despite the reasonable methane oxidation activity exhibited by the large particles, the initial PdO particles could potentially provide a 40 °C lower methane oxidation temperature. In the presence of water in the feed at moderate temperature (450°C), support degradation governs the deactivation of the catalyst, which is evidenced by a significant decrease in BET surface area and generation of extra-framework aluminium species. These results suggest that active and stable catalysts could be obtained by careful choice and design of the support material with the aim to guarantee high dispersion of PdO.

Keywords: methane oxidation, exhaust aftertreatment, palladium, zeolite, deactivation, ageing

1. Introduction

Natural gas, which consists primarily of methane, is a promising midterm fuel to significantly reduce carbon dioxide emissions due to its advantageous hydrogen-to-carbon ratio, established usage applications, abundance, available world-wide reserves and distribution network, and the possibility to produce it from renewable sources (bio-gas). Lean-burn natural gas engines are very efficient and allow to significantly reduce CO₂, NO_x and CO emissions compared to gasoline and diesel engines. However, considerable amounts of methane remain unburnt especially under lean conditions and are emitted at concentrations of several thousand ppm. This causes environmental concerns as methane possesses about 20 times larger global warming potential than CO₂. Hence, lean methane abatement requires an efficient and stable methane oxidation catalyst [1-5].

Several reports showed Pd/zeolite catalysts to be promising candidates to substitute conventional Pd/Al₂O₃ catalysts due to their high activity and ability to convert methane at lower temperature [6-15]. ZSM-5 and mordenite are the most commonly studied zeolite frameworks [7,9-11]. From a comparison of methane oxidation on various zeolite-based catalysts over a broad range of palladium loadings (1.2 to 4 wt. % Pd) and Si/Al ratios (7 to 27) it was concluded that the highest reaction rate is reached on the STI-type framework followed by MFI, BEA and MOR [13]. A study with low palladium loadings (0.1 to 0.3 wt. %) indicated that high Si/Al ratio is generally favorable to obtain more active and stable catalysts irrespective of the zeolite framework [9,11,12]. M'Ramadj et al. [8] compared the acidity of Pd/Al₂O₃ and Pd/ZSM-5 prepared with different methods and concluded that strong Brönsted acidity was crucial for methane activation at low temperature. Among various preparation methods, ion-exchange of palladium ammine complex yielded higher palladium dispersion and initial activity [9].

Despite the significant number of studies on methane oxidation over Pd/zeolite catalysts, very limited structural data is available on their ageing behavior and the course of deactivation. Activity and resistance to deactivation in the presence of water are serious issues for zeolite catalysts for methane oxidation. Several authors [9,14,16] performed stability tests on various catalysts, but characterization of the spent catalysts was not provided. Okumura et al. [11,12] measured Pd K-edge EXAFS of ZSM-5 and mordenite supported palladium before and after reaction and concluded PdO sintering to be the reason for the observed deactivation. However, the structural properties of the corresponding supports were not provided, thus leaving the role of the support in the deactivation of the catalyst ambiguous. A comprehensive study of the deactivation process of catalysts based on palladium and zeolites comprising characterization of both the support and the active phase would be helpful for the design of an active and stable Pd/zeolite methane oxidation catalyst.

In this work, the evolution of the structure of Pd/ZSM-5 in the reaction conditions, including also the presence of steam in the feed, was investigated with a focus on both the metal active phase and the zeolite support using nitrogen adsorption, solid-state nuclear magnetic resonance, powder X-ray diffraction, transmission electron microscopy and X-ray absorption spectroscopy.

2. Experimental

2.1. Catalyst synthesis

ZSM-5 zeolite in Na-form with Si/Al=20 (Zeocat PZ-2/40) was kindly supplied by Zeochem. The zeolite was calcined at 600 °C prior to the catalyst synthesis. The calcined zeolite (4 g) was ion-exchanged three times with NH_4NO_3 (1M, 20 ml) and calcined at 600 °C to obtain the H-form. H-ZSM-5 was then ion-exchanged at room temperature for 24 h with the required amount of $[\text{Pd}(\text{NH}_3)_4](\text{NO}_3)_2$ solution (pH = 9) to obtain 1 wt. % loading of

palladium. After drying at 120 °C for 12 h, the Pd/H-ZSM-5 catalyst was obtained by calcination at 500 °C for 2 h. This sample was labelled as “calcined”. The heating rate was set to 2 °C/min to obtain highly dispersed PdO nanoparticles [17-19].

2.2. Catalyst activity evaluation

Evaluation of the catalytic activity and stability was carried out using the catalyst in powder form in a dedicated setup comprising a quartz-glass plug flow reactor (ID = 6 mm), gas flowmeters, heating control and a gas analysis system (InProcess Instruments GAM 400 mass spectrometer). Fragments with the m/z ratio of 2 (H₂), 12 (C), 15 (CH₄), 16 (O₂), 18 (H₂O), 28 (N₂), 30 (NO), 32 (O₂) and 44 (CO₂) were followed. The catalyst (50 mg, 150-200 µm sieve fraction) was mixed with cordierite (150 mg, 100-150 µm) to mitigate the exothermic effect of the reaction and was then fixed firmly in the reactor between two quartz wool plugs. Methane conversion curves were taken at the heating/cooling rate of 10, 20 and 50 °C/min in the feed comprising 1 vol. % CH₄, 4 vol. % O₂, N₂ balance (GHSV = 80'000 h⁻¹). The first ascending ramp was taken from 200 °C to 550 °C, followed by stabilization of the catalyst at 550 °C for 30 min. Then, the reactor was cooled to 300 °C and the heating/cooling sequence to 550 °C was repeated twice without waiting at 550 °C to ensure that the catalyst had stabilized and the data obtained was reproducible. After this treatment, the catalyst was labelled as “stabilized catalyst”. Isothermal activity tests were performed upon introduction of the reaction feed at 325, 360 or 390 °C without pre-treatment. Hydrothermal stability was tested at constant temperature (450 °C) with the addition of 5 vol. % of steam to the feed. Alternately, steam was added to and removed from the feed at intervals of 60 min at the same temperature in a separate experiment. No other products than CO₂ and H₂O were detected during all activity tests.

2.3. Catalyst characterization

The palladium loading as well as the Si:Al:Na ratio of the starting material and the final catalyst were determined by inductively coupled plasma mass spectrometry (ICP-MS) using an Agilent 7700x ICPMS instrument after complete digestion of the samples in the HCl/HNO₃/HF mixture (ratio 6:3:1) in a 3000 Anton Paar microwave digestion unit. The zeolite crystallinity and the presence of the PdO phase were confirmed by powder X-ray diffraction (XRD) using a Bruker D8 Advance AXS diffractometer with Cu K α radiation in the 2 θ range from 10° to 60°. Scanning transmission electron microscopy (STEM) images were taken with a Hitachi HD-2700 microscope at the 200 kV acceleration voltage. Extended X-ray adsorption fine structure (EXAFS) data were measured at the Pd K-edge (24.35 keV) in transmission mode on pelletized samples at the SuperXAS beamline of the Swiss Light Source (SLS, Paul Scherrer Institut). The Fourier transformation of the k²-weighted EXAFS functions was performed the range 3–12 Å⁻¹ [20]. Data reduction was performed using the Athena software package [21]. Solid-state magic angle spinning nuclear magnetic resonance (MAS NMR) ²⁷Al spectra were recorded at 10 kHz collecting 2048 accumulations on a Bruker Avance 400 MHz spectrometer with ammonium aluminium sulfate dodecahydrate (AlNH₄(SO₄)₂·12H₂O) as reference. The textural properties of the support were obtained from nitrogen physisorption measurements at 77 K using a Quantachrome Autosorb 1 instrument. Prior to the measurement the samples were degassed for 6 h at 200°C to remove water and other adsorbed species. The specific surface area was calculated using the Brunauer–Emmett–Teller (BET) method. The micropore volume and micropore surface area were calculated from the t-plot.

3. Results and discussion

3.1. Catalyst stabilization

Table 1 shows the chemical composition of the support and the final catalyst determined by ICP-MS. The Si/Al ratio was found to be 20.2 which is in accordance with the supplier specifications. The Na/Al ratio in the original zeolite was much lower than 1, indicating that the zeolite was initially in the mixed Na-H form. The decrease in Na/Al ratio from 0.22 to 0.07 confirmed that most of the sodium was removed from the final catalyst by the repeated exchange with ammonium nitrate followed by calcination. The palladium loading was 0.88 wt. %, which was slightly lower than the expected value.

Figure 1 shows methane oxidation profiles of the Pd/H-ZSM-5 catalyst obtained during the first ascending ramp at the three different heating rates (10, 20 and 50 °C/min). The observed conversion gradually increased with the increasing heating rate in the region between 250 and 450 °C and remained almost identical above 450 °C for the three ramp rates. After operation at 550 °C for 30 min and subsequent repetition of the heating/cooling sequence, the methane oxidation profile of the stabilized catalyst exhibited lower activity below 375 °C than that obtained in the ascending ramps for the different heating rates. Above ca. 375 °C, the activity was slightly better.

When methane was introduced to the feed at the temperature higher than 200 °C, i.e. at 325, 360 and 390 °C (filled symbols in Figure 1), the initial conversion was significantly higher than that of the stabilized catalyst. However, the activity returned to the value measured for the stabilized catalyst within the 30 min of isothermal operation at those temperatures.

The excess amount of methane converted during the first ascending ramp compared to the following runs between 250 °C and 450 °C (about 2 mmol) was significantly larger than the amount of palladium in the catalyst bed (0.072 mmol) while no other reaction products were detected. This indicates that the higher conversion observed in the first run and in the subsequent isothermal runs is catalytic and occurred neither due to a stoichiometric reaction nor to precursor decomposition. Such behavior suggests that the calcined catalyst was

initially very active, but then changed rapidly and irreversibly in the reaction environment. It is likely that the activity changes originate from modification of the structure of the active phase and/or of the zeolite support.

Therefore, the calcined catalyst and the catalyst obtained at 360 °C after the 30 min run were characterized by scanning transmission electron microscopy (STEM, Figure 2). A slow calcination program should ensure that the palladium objects remain well dispersed on the zeolite support [17-19]. In fact, the calcined Pd/H-ZSM-5 exhibited well-dispersed palladium nanoparticles of 1-2 nm diameter (Figure 2a). Although this is larger than the ZSM-5 micropore diameter of 0.55 nm, such particles are likely located within the zeolite structure [22]. The image of the catalyst obtained after contact with the feed at 360°C shows that these particles already aggregated achieving a final size between 5 and 10 nm (Figure 2b). We speculate that the aggregation was induced by the presence of methane, since the particles of 1-2 nm are the result of calcination in air at higher temperature. The rather irregular morphology of the large objects observed after reaction together with the ramification of many particles encourage to think that particle growth derives from the high mobility of the small palladium particles on the support. The significant change in dispersion was also observed by X-ray diffraction (XRD, Figure 3). The reflection at $2\theta = 33.8^\circ$ attributed to the PdO phase [23-25] was not detected in the pattern of the calcined catalyst thus confirming its high metal dispersion, but it appeared in the spent catalyst. Figure 4 shows the Fourier transform of the palladium K-edge EXAFS spectrum of the calcined sample. Besides the first Pd-O coordination shell (ca. 1.5 Å), a less intense contribution from the Pd-O-Pd shell (ca. 3 Å) than in the PdO reference was also present, which suggests that palladium was in the oxidized state in the calcined catalyst. Although no metallic palladium species were detected by XRD and EXAFS, the question whether the initial PdO particles undergo some extent of reduction during the sintering process under these conditions will need to be answered by in

situ observation of the palladium oxidation state [26,27], which is beyond the scope of this work. Figure 3 also demonstrates that the reflections corresponding to ZSM-5 did not change indicating that the zeolite crystal structure remained intact during the experiment.

Figure 5 shows ^{27}Al MAS NMR spectra of Na-ZSM-5, calcined Pd/H-ZSM-5 and the spent catalyst operated at 360 °C for 30 min. Two distinct peaks were observed at around 0 and 55 ppm chemical shift. The latter signal corresponds to the tetrahedral framework aluminium (Al_T) while the former to the framework-associated octahedral aluminium (Al_oct). Additionally, framework aluminium distortions are typically recognized from the broadening and shift to lower values of the Al_T feature that produces an asymmetric peak [25,28]. Compared to the Na-ZSM-5 material the calcined and spent Pd/H-ZSM-5 catalysts exhibited a slight increase in the framework aluminium distortion and the corresponding Al_T peak shifted from 54.3 ppm to 53.8 ppm and 53.7 ppm, respectively.

Textural properties of the parent Na-ZSM-5, calcined Pd/H-ZSM-5 and spent Pd/H-ZSM-5 obtained from nitrogen physisorption are given in Table 2. Specific surface area and micropore volume of the spent catalyst slightly decreased compared to the calcined catalyst indicating that the zeolite structure was not affected by exposure to the reaction mixture. PdO particle sintering observed by STEM and XRD together with only minor changes in the support material detected by ^{27}Al MAS NMR and nitrogen physisorption indicate that the support was stable under reaction conditions. Therefore, we consider that the loss of initial activity was induced solely by PdO nanocluster sintering.

Despite its initial deactivation, Pd/H-ZSM-5 was still very active in methane oxidation, exhibiting 50% methane conversion (T_{50}) below 400 °C. However, if the PdO nanoparticles would remain at the dispersion level of the calcined Pd/H-ZSM-5 catalyst, the activity would be even higher, as it is suggested by the dotted line in Figure 1. This curve is the methane oxidation profile obtained by joining the first points of the isothermal experiments (Figure 1,

black arrows). Such a catalyst would provide a shift of T_{50} by about 40 °C to lower values compared to the stabilized one.

3.2. Ageing in the presence of steam

It is well-known that steam has a detrimental effect on the activity of Pd/zeolite catalysts significantly decreasing their lifetime [10,12,13]. To study catalyst degradation over time, Pd/H-ZSM-5 was exposed to the reaction mixture with the addition 5 vol. % of steam at 450 °C for 1, 4, 8 and 16 h and was then characterized by STEM, nitrogen physisorption, ^{27}Al MAS NMR spectroscopy and XRD. To compare the deactivation rate in dry and wet feed, a test with repeated addition and removal of 5 vol. % of steam was also performed. Figure 6 depicts the activity decrease of Pd/H-ZSM-5 for methane oxidation under these conditions. In the case of the constant wet feed, rapid deactivation of the catalyst occurred immediately after water was added, resulting in loss of two thirds of the initial activity in the first 4 hours. The rapid deactivation phase was followed by a slower phase where the conversion dropped from 25 to 10% in 12 hours. Methane conversion followed the same trend for all samples thus showing good reproducibility of the ageing experiments. When steam was repeatedly added to and removed from the feed every 60 min, the deactivation rate in the wet feed segment was similar to that in the constant wet feed mode, but the overall deactivation rate of the catalyst over time on stream slowed down. Upon the addition of steam an instant loss of methane conversion occurred, which confirms the sensitivity of the Pd/H-ZSM-5 system to water. Activity also recovered very quickly when steam was removed from the feed and no loss of activity was observed in the dry feed segment. However, methane conversion never returned to the level of the previous segment in dry feed, suggesting irreversible deactivation of the catalyst.

XRD patterns of the calcined catalyst and of that aged in the presence of steam are presented in Figure 7. No significant difference in the intensity of peaks corresponding to ZSM-5 was observed confirming that the support remained crystalline after ageing. The PdO phase ($2\theta = 33.8^\circ$), which could not be detected in the calcined catalyst due to its high dispersion (Figure 3b), appeared in the diffractograms of all samples exposed to steam showing sintering of the PdO nanoparticles.

Despite the absence of significant changes in the diffraction patterns of the support, the textural properties experienced measurable variations. Table 3 shows the results of nitrogen physisorption experiments. Both the specific surface area and the micropore volume of Pd/H-ZSM-5 decreased with increasing ageing time, thus revealing the gradual degradation of the zeolite pore structure.

Figures 3 and 5 illustrate the superior sensitivity of NMR spectroscopy to structural changes of the zeolite framework compared to XRD and it was thus exploited to characterize the aged samples. Figure 8 shows ^{27}Al MAS NMR spectra of calcined and aged catalysts. The Al_{oct} signal (0 ppm) only slightly increased with increasing ageing time. More pronounced changes were observed for the Al_{T} signal, which gradually shifted from 53.8 ppm for the calcined catalyst to 52.2 ppm for the sample aged for 16 hours. The peak broadening observed in the region from 50 to 20 ppm indicated the relative increase in the amount of distorted aluminium species [25,28], thus demonstrating the framework degradation that could not be observed by XRD. The data provided evidence of significant degradation of the zeolite framework under reaction conditions in wet feed at mild temperatures, which is known to severely limit the temperature range of application of zeolite-based catalysts.

STEM images of the sample aged for 16 h further confirmed the data obtained by XRD, NMR and nitrogen physisorption measurements. Figures 9(a) and 9(b) show large and irregular PdO nanoparticles with sizes ranging from tens to hundreds of nm. PdO particle size

distribution statistics shown in Figure 9(c) suggest that the addition of steam to the feed lead to the formation of even larger PdO particles than in dry feed, which was likely accelerated by the zeolite degradation.

4. Conclusions

Deactivation of Pd/H-ZSM-5 in methane oxidation was studied by characterizing both the active phase and the zeolite support. ZSM-5 zeolite with Si/Al ratio 20 is unable to stabilize one to two nanometer PdO nanoparticles upon exposure to the reaction mixture. As a consequence, the metal sinters to 5 to 10 nm nanoparticles, which are then active and stable in dry reaction conditions. The zeolite support remains stable during this process. The initial highly dispersed PdO nanoparticles of the calcined catalyst provide around 40 °C lower temperature of 50% methane oxidation compared to the stabilized catalyst. This implies that Pd/ZSM-5 has a great potential in methane oxidation, which could be realized by preserving the initial dispersion of the palladium active phase.

Ageing of the catalyst in a feed containing water reveals partial zeolite collapse. Although the long-range structure of the support was preserved, a significant loss of surface area and an increase in Al distortion were observed by nitrogen physisorption and ^{27}Al MAS NMR spectroscopy. The average PdO particle size was significantly larger than in the dry feed suggesting that support degradation contributes to the sintering of PdO particles in the wet feed. Hence, the zeolites that are more resistant to steaming are favored for the design of a hydrothermally stable methane oxidation catalyst.

Acknowledgements

The authors would like to thank the Paul Scherrer Institut for financial support and for granting access to SLS, Dr. F. Krumeich (ETH Zurich) for the electron microscopy images,

Dr. R. Verel (ETH Zurich) for assistance with NMR measurements and Dr. M. Nachtegaal (PSI) for his support with XAS measurements.

References

1. Choudhary TV, Banerjee S, Choudhary VR (2002) Catalysts for combustion of methane and lower alkanes. *Appl Catal A: General* 234:1-23
2. Gelin P, Primet M (2002) Complete oxidation of methane at low temperature over noble metal based catalysts: a review. *Appl Catal B: Environmental* 39:1-37
3. Gonzalez-Velasco JR, Botas JA, Gonzalez-Marcos JA, Gutierrez-Ortiz MA (1997) Influence of water and hydrocarbon processed in feedstream on the three-way behaviour of platinum-alumina catalysts. *Appl Catal B: Environmental* 12:61-79
4. Lampert JK, Kazi MS, Farrauto RJ (1997) Palladium catalyst performance for methane emissions abatement from lean burn natural gas vehicles. *Appl Catal B: Environmental* 14:211-223
5. Lee JH, Trimm DL (1995) Catalytic combustion of methane. *Fuel Process Technol* 42:339-359
6. Kalantar Neyestanaki A, Kumar N, Lindfors LE (1995) Catalytic combustion of propane and natural gas over Cu and Pd modified ZSM zeolite catalysts. *Appl Catal B: Environmental* 7:95-111
7. Li Y, Armor JN (1994) Catalytic combustion of methane over palladium exchanged zeolites. *Appl Catal B: Environmental* 3:275-282
8. M'Ramadj O, Li D, Wang X, Zhang B, Lu G (2007) Role of acidity of catalysts on methane combustion over Pd/ZSM-5. *Catal Commun* 8:880-884
9. Maeda H, Kinoshita Y, Reddy KR, Muto K, Komai S, Katada N, Niwa M (1997) Activity of palladium loaded on zeolites in the combustion of methane. *Appl Catal A: General* 163:59-69
10. Montes de Correa C, Villa AL (1996) Combustion of methane over palladium ZSM-5 and mordenite catalysts. *Appl Catal B: Environmental* 10:313-323

11. Okumura K, Matsumoto S, Nishiaki N, Niwa M (2003) Support effect of zeolite on methane combustion activity of palladium. *Appl Catal B: Environmental* 40:151-159
12. Okumura K, Shinohara E, Niwa M (2006) Pd loaded on high silica beta support active for the total oxidation of diluted methane in the presence of water vapor. *Catal Today* 117:577-583
13. Park JH, Kim B, Shin CH, Seo G, Kim SH, Hong SB (2009) Methane combustion over Pd catalysts loaded on medium and large pore zeolites. *Top Catal* 52:27-34
14. Shi C, Yang L, Cai J (2006) Cerium promoted Pd/HZSM-5 catalyst for methane combustion. *Fuel* 86:106-112
15. Shi C, Yang L, Wang Z, He Z, He X, Cai J, Li G, Wang X (2003) Promotion effects of ZrO₂ on the Pd/HZSM-5 catalyst for low-temperature catalytic combustion of methane. *Appl Catal A: General* 243:379-388
16. Zhang B, Wang X, M'Ramadj O, Li D, Zhang H, Lu G (2008) Effect of water on the performance of Pd-ZSM-5 catalysts for the combustion of methane. *J Nat Gas Chem* 17:87-92
17. Homeyer ST, Sachtler WMH (1989) Elementary steps in the formation of highly dispersed palladium in NaY. *J Catal* 117:91-101
18. Zhang Z, Mestl G, Knözinger H, Sachtler WMH (1992) Effects of calcination program and rehydration on palladium dispersion in zeolites NaY and 5A. *Appl Catal A: General* 89:155-168
19. Pommier B, Gelin P (1999) On the nature of Pd species formed upon exchange of H-ZSM-5 with Pd(NH₃)₄²⁺ and calcination in O₂. *Phys Chem Chem Phys* 1:1665-1672
20. Lamberti C, van Bokhoven J (2016) X-Ray Absorption and Emission Spectroscopy for Catalysis. In: van Bokhoven J, Lamberti C (eds) *X-ray Absorption and X-ray Emission Spectroscopy: Theory and Applications*. John Wiley & Sons

21. Ravel B, Newville M (2005) ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. *Journal of Synchrotron Radiation* 12 (4):537-541. doi:10.1107/S0909049505012719
22. Zecevic J, van der Eerden MJ, Friedrich H, de Jongh PE, de Jong KP (2013) Heterogeneities of the Nanostructure of Platinum/Zeolite Y Catalysts Revealed by Electron Tomography. *ACS Nano* 7:3698-3705
23. Domingos D, Simplicio LMT, Estrela GS, dos Prazeres MAG, Brandao ST (2007) Catalytic combustion of methane over PdO-CeO₂/Al₂O₃ and PdO-CeO₂/ZrO₂ catalysts. *Stud Surf Sci Catal* 167:7-12
24. Jablonska M, Krol A, Kukulska-Zajac E, Tarach K, Chmielarz L, Gora-Marek K (2014) Zeolite Y modified with palladium as effective catalyst for selective catalytic oxidation of ammonia to nitrogen. *J Catal* 316:36-46
25. Pinar AB, Verel R, Perez-Pariente J, van Bokhoven JA (2014) Direct evidence of the effect of synthesis conditions on aluminum siting in zeolite ferrierite: A ²⁷Al MQ MAS NMR study. *Micropor Mesopor Mat* 193:111-114
26. Grunwaldt JD, van Vegten N, Baiker A (2007). *Chem Commun*:4635-4637
27. Matam SK, Aguirre MH, Weidenkaff A, Ferri D (2010) Revisiting the Problem of Active Sites for Methane Combustion on Pd/Al₂O₃ by Operando XANES in a Lab-Scale Fixed-Bed Reactor. *J Phys Chem C* 114:9439-9443
28. Yan Z, Ma D, Zhuang J, Liu X, Han X, Bao X, Chang F, Xu L, Liu Z (2003) On the acid-dealumination of USY zeolite: a solid state NMR investigation. *J Mol Catal A-Chem* 194:153-167

Figure captions

Figure 1. Methane conversion profiles of Pd/HZSM-5 in the first ascending ramp at 10 ($\square$), 20 ($\circ$) and 50 $^{\circ}\text{C}/\text{min}$ ($\triangle$) rate and in isothermal runs at 325, 360 and 390 $^{\circ}\text{C}$ ($\bullet$, and arrows). The continuous black curve corresponds to the activity obtained after operating the catalyst at 550 $^{\circ}\text{C}$ for 30 min followed by two subsequent heating/cooling ramps (stabilized catalyst). The dotted curve is used to guide the eyes.

Figure 2. STEM images of Pd/H-ZSM-5 (a) calcined and (b) after the 30 min run at 360 $^{\circ}\text{C}$.

Figure 3. XRD patterns of (a) Na-ZSM-5, (b) Pd/H-ZSM-5 calcined at 500 $^{\circ}\text{C}$ and (c) spent Pd/H-ZSM-5 operated at 360 $^{\circ}\text{C}$ for 30 min. The patterns are offset for clarity. Inset: 2θ range 32-36 $^{\circ}$ for (b) and (c).

Figure 4. Fourier transforms of non-phase shifted k^2 -weighted Pd K-edge EXAFS spectra of calcined Pd/H-ZSM-5 and PdO reference.

Figure 5. ^{27}Al MAS NMR spectra of Na-ZSM-5, calcined Pd/H-ZSM-5 and spent Pd/H-ZSM-5 operated at 360 $^{\circ}\text{C}$ for 30 min.

Figure 6. Time dependence of methane conversion on Pd/H-ZSM-5 at 450 $^{\circ}\text{C}$ with constant and periodic addition of steam to the feed. Feed composition: 1 vol. % CH_4 , 4 vol. % O_2 , 0 or 5 vol. % H_2O , bal. N_2 .

Figure 7. XRD patterns of Pd/H-ZSM-5: (a) calcined and aged in wet reaction feed at 450 °C for (b) 1, (c) 4, (d) 8 and (e) 16 hours. Patterns are offset for clarity. Inset: 2θ range 32-36°

Figure 8. ^{27}Al MAS NMR spectra of Pd/H-ZSM-5: (a) calcined and (b-e) aged at 450 °C for 1, 4, 8 and 16 hours in wet reaction feed. The vertical line is used to guide the eyes. Spectra are offset for clarity.

Figure 9. (a,b) STEM images of Pd/H-ZSM-5 aged at 450 °C for 16 h in wet reaction feed and (c) PdO particle size distribution in Pd/H-ZSM-5: calcined, spent in dry feed at 360 °C for 30 min and aged in wet feed at 450 °C for 16 h. The size distribution is the result of counting ca. 700, 180 and 100 particles, respectively.

Table 1. Chemical composition of Na-ZSM-5 and the calcined Pd/H-ZSM-5 catalyst determined by ICP-MS.

Sample	Na-ZSM-5		Pd/H-ZSM-5	
	Conc. (wt. %)	RSD (%)	Conc. (wt. %)	RSD (%)
Na	0.36	0.47	0.12	3.01
Al	1.89	0.42	1.88	0.82
Si	39.6	0.24	39.3	0.92
Pd	0.00	n/a	0.88	0.97
Si/Al	20.2		20.1	
Na/Al	0.22		0.07	

Table 2. Specific surface area and micropore volume of Na-ZSM-5, calcined Pd/H-ZSM-5 and spent Pd/H-ZSM-5 operated at 360 °C for 30 min

Sample	BET surface area (m²/g)	Micropore surface area (m²/g)	External surface area (m²/g)	Micropore volume (cm³/g)
Na-ZSM-5	533	287	246	0.119
Pd/H-ZSM-5	507	275	232	0.115
spent Pd/H-ZSM-5	494	265	229	0.109

Table 3. BET specific surface area and total pore volume of calcined and aged Pd/H-ZSM-5.

Ageing time	BET surface	Micropore surface	External surface	Micropore
(h)	area (m²/g)	area (m²/g)	area (m²/g)	volume (cm³/g)
0	507	275	232	0.115
1	481	256	225	0.107
4	420	239	181	0.099
8	382	218	164	0.090
16	346	197	149	0.082