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Catalytic combustion of ventilation air methane (VAM) – long term catalyst stability in the presence of water vapour and mine dust

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In this paper we report new insights into the deactivation phenomena of palladium based catalysts for catalytic combustion of ventilation air methane (VAM). It was found that the primary factor responsible for low temperature catalyst deactivation is the water vapour present in the feed stream. The influence of water vapour on VAM was examined by comparing the properties of fresh-catalysts with catalysts following over 1000 h reaction time on stream. The techniques applied to characterize the catalysts included TPD, XRD, N₂-isotherm adsorption, H₂-chemisorption and XPS analyses. Alternating between dry and water vapour-saturated VAM feed disclosed ca. 50 % reversible drop in activity. XPS analysis suggests an absence of a palladium hydroxide phase during the initial 2 h on stream, although prolonged exposure to reactant leads to the formation of palladium hydroxide, which appears to match the progressive deactivation of the Pd/Al₂O₃ catalyst. Introducing VAM dust (a mixture of fine coal, CaCO₃ and aluminosilicate particles) causes a variation in catalytic activity originating from coal-dust ignition and the effect of chloride on the surface of catalyst. In the presence of these inhibiting agents, an average methane conversion of higher than 75 % over 1100 h was achieved at reaction temperatures below 600 °C.

Introduction

Concerns over the rising concentration of greenhouse gases in the atmosphere have generally focused on carbon dioxide, although there is a growing emphasis on lowering methane emissions. Methane has been assigned a CO₂ greenhouse gas warming potential (GWP) of 25 over a 100 year time horizon,¹ and the conversion of CH₄ to CO₂ is considered as a potentially viable approach to reduce net emissions of greenhouse gases. Underground ventilation air systems in "gassy" coal mines contribute significantly to net methane emissions, although the

concentration of methane in the ventilation air stream is typically below 1 %. The high volumetric flow rates (typically 300 m³.s⁻¹) and the subsequent net discharge of significant quantities of methane have generated interest in developing technologies to reduce VAM emissions.² As reported in the literatures,^{3,4} besides air and methane, the VAM stream usually contains water (relative humidity = 70-100 %), CO₂ (<2.5 %), coal dust and others particles (such as calcium oxides, iron oxides, clay and quartz at dust loading range of 0.1-4.5 mg.m⁻³). It may also contains traces of CO, C₂H₆ (higher

hydrocarbons), He, H₂, HCN, NH₃, NO_x, H₂S, and SO₂ (organic sulphur compounds).

Basically, mitigation and utilization technologies of VAM are classified into two categories, ancillary uses and principal uses.^{5, 6} For the ancillary uses, the VAM gas is used as combustion air for boilers, turbines and internal combustion engines while for principal uses the VAM is oxidized in a reactor to burn methane emission as well as produce the energy. One potential technological solution for treatment of ventilation air methane (VAM) is catalytic combustion, where methane is oxidized to carbon dioxide on a catalytically active solid surface. This flameless combustion is ideal for highly diluted air-methane streams, such as VAM, as the concentration of methane is outside the typical flammability range for methane in air. Production of NO_x is essentially absent and the reaction temperature is relatively low (generally below 500 °C).

The catalytic oxidation of methane at low temperature has been extensively investigated, especially over Pd and Pt based catalysts. A comprehensive review of methane oxidation over noble metal based catalysts agrees that, the supported Pd catalysts are the most active materials.⁷ However, palladium catalysts can be susceptible to poisoning by water vapour and other contaminants, which may result in severe deactivation when used in the catalytic combustion of VAM. Many recent investigations are focused on catalyst modifications which aim to enhance the durability of catalysts, especially developing resistance against water, sulfur compounds and particulates, as well as enhancing the absolute activity of the catalyst.⁷

Although it is well recognised that water vapour strongly inhibits the activity of catalysts, the mechanism of catalyst deactivation is uncertain.⁸ Some earlier studies reported that, the water produced by reaction significantly inhibits the activity of Pd/Al₂O₃ at lower temperatures due to competition with methane for active sites.⁹⁻¹¹ Furthermore, irreversible deactivation can be induced by the presence of water vapour where the active site (PdO) transforms into a less active site (palladium hydroxide).⁹⁻¹² The rate of Pd/Al₂O₃ catalyst deactivation in the presence of water, either present in the feed (such as the case in VAM) or produced in the catalytic combustion reaction, is heavily dependent on reaction temperature.^{10, 12} The inhibiting effect of water is more significant at lower temperatures, becoming less apparent at temperatures higher than 450 °C.¹⁰ Ciuparu et al. suggested that, the hydroxyl groups produced by the reaction are bound strongly on the surface and when additional external water is introduced, the surface becomes saturated and the rate of desorption of water from the surface of the catalyst is slowed due to the high concentration of water vapour in the feed and product streams.¹³ Recent work by Schwartz et al. proposes an alternative explanation regarding deactivation of palladium supported on various metal oxides.^{8, 14} They suggest that hydroxyl groups formed during the reaction accumulate on the catalyst support and inhibit the rate of exchange of oxygen between the support and PdO,¹⁴ a process which is necessary for surface reaction. This accumulation of hydroxyl groups prevents the migration of oxygen from the support to the Pd

active site, as well as reducing the availability of oxygen involved in the oxidation of methane.⁸ Clearly the primary mechanisms leading to deactivation is contentious, as it is possible that hydroxyls form on both the Pd site and the support in high concentration⁸ and deactivation can potentially originate from surface on either the support or palladium. Recently Di Carlo and co-workers reported improved tolerance against water poisoning in catalytic combustion of methane over palladium catalysts by using a support which inhibited or delayed the reaction between Pd and H₂O,¹⁵ however no long time stability test results were reported.

The application of a catalytic process for VAM abatement requires long-term evaluation of the catalyst stability and durability under humid feed condition. There are a limited number of reports on the hydrothermal stability tests of supported palladium catalysts. Yamamoto and Uchida reported longer-lasting hydrocarbon oxidation activity over Pt and Pd supported on alumina for lean-burn natural gas engine exhausts¹⁶ where the total hydrocarbon conversion dropped from 80 % to 50 % within 2500 h at 385 °C. Enhanced hydrothermal stability data during 3200 h methane oxidation at 600 °C was published recently by Liu and co-workers.¹⁷ Hydrothermal stability of the catalyst was improved by optimizing the Ni/Al ratio for Ni supported alumina catalysts. Notwithstanding, stability data was not reported at reaction temperatures less than 600 °C or the effect of CO₂ in the feed for long term catalyst stability tests. In addition, to our knowledge, there is no literature reporting on the effect of coal mine dust on the catalytic combustion of ventilation air methane.

In this paper, we report the effect of water and coal mine dust present on supported palladium catalysts during the catalytic combustion of a surrogate VAM gas. Attempts to improve the resistance of catalysts are explored by determining differences in the physical and chemical characteristics of this catalyst (fresh and following long term activity testing). The stability of the Pd catalysts are evaluated for a long term activity under simulated ventilation air methane (where the feed contains components such as CH₄, CO₂, H₂O and air) in order to understand the deactivation phenomena of Pd/Al₂O₃ catalyst over a long period of time. The effect of coal mine dust is assessed by adding it to the catalyst and noting any effect it has on catalyst activity and stability. The combustion tests are operated under conditions where the level of methane conversion is maintained at or above 90 % by increasing the catalyst bed temperature.

Experimental

Catalyst preparation

Catalyst containing 1.2 wt% Pd/Al₂O₃ was prepared by wet impregnation of alumina (gamma and delta Al₂O₃, Chem-Supply) support with an aliquot of Pd (II) nitrate solution (10 wt% in 10 wt% nitric acid, Sigma-Aldrich) mixed using a mortar and pestle. Water was added drop-wise while mixing,

until a paste was formed. The resulting paste was dried in the oven at 110 °C for approximately 20 h. The dried catalyst was then ground, pressed and sieved to 250-400 µm. A tubular fixed-bed reactor employed for calcination of dried solid catalyst in air at 500 °C for 1 h followed by purging in helium for 30 min. For activation, the sample was reduced in H₂ at 300 °C for approximately 2 h and subsequently purged with helium while slowly heating the catalyst to desired reaction temperature. For long-term stability experiments, we use a commercially available 1.0 wt% Pd/Al₂O₃ (Sigma-Aldrich) and activated it in air at 500 °C for 4 h followed by purging in H₂ for 2 h.

Catalyst characterization

The surface area of catalysts was measured by nitrogen adsorption at 77 K using Gemini 11 2370 surface area analyzer. Micromeritics 2910 AutoChem (Micromeritics Instruments Corp., USA) assessed the active particle size and metal dispersion by performing a number of H₂ pulse-chemisorption. Temperature-programmed desorption (TPD) analysis was carried out using a purpose built TPD apparatus with a Pfeiffer Prisma quadrupole mass analyser for detection. Transmission Electronic Microscopy (TEM) images of the sample served to capture by JEOL 2100. Palladium loading was quantified using Varian 715-ES inductively coupled plasma optical emission spectrometer (ICP-OES). Powder X-Ray diffraction patterns of catalysts and ventilation air dust were examined using Cu K α radiation with a Philips X'Pert diffractometer. Diffractograms were collected in the 2 θ angle range from 2° to 90° with 0.008° 2 θ step resolution.

For surface analysis, ex-situ X-ray photoelectron spectroscopy (XPS) was carried out using monochromated Al K alpha (energy 1486.68 eV) radiation and the emitted photoelectrons were analyzed using an ESCALAB250Xi manufactured by Thermo Scientific, UK. To minimize the possibility of sample contamination, spent samples were immediately transferred into sealed containers after stopping the reaction by cooling in helium. The sample was mounted on the stub using indium tape. The energy in the XPS spectra was referenced to the adventitious carbon adsorption at 284.6 eV. The shift was cross checked with the position of O 1s from Al₂O₃ which is found at 531eV.

Catalytic activity measurement

The activity of the catalyst was measured in a tubular stainless steel micro reactor. The reactant mixture composition was varied in the range of 0.6-0.8 % of CH₄ balanced with air at various flow rates. The inlet and outlet mixtures were analyzed using a gas chromatograph equipped with a thermal conductivity detector (TCD) and concentric-packed single column (Alltech CTR-I). For humid feed experiments, the reactant mixture was passed through a saturator and a humidity probe (HumidiProbe, Pico Technology Ltd.) was installed at the outlet. The reaction temperature was measured with a thermocouple placed into the catalyst bed. At constant water vapour pressure, the repeatability of the data is 3.8 %.

For catalytic stability studies, a second, separate reactor set-up was used and operated continuously with varying conditions (temperature was increased in order to maintain a 90 % level of conversion for methane). Throughout the study, the feed concentration of methane and carbon dioxide were kept constant at 7000 ppm and 10 000 ppm, respectively. During this experiment, our calculation on the total carbon at the inlet and outlet reactor results in average carbon balance of 96 %. The average water content was measured at approximately 85 % relative humidity (RH) for the saturator system used ($T = 28 \text{ °C} \pm 3 \text{ °C}$, ambient), corresponding to a H₂O_(v) pressure of approximately 32 000 ppm. As reported in the literature,⁴ the relative humidity of VAM stream is fluctuated, ranging from 70 % to 100 % RH. Thus, our saturator system was aimed producing humidity within this range. The feed gas hourly space velocity (GHSV) was maintained at 100 000 h⁻¹ for the majority of the tests, although in a limited number of tests the GHSV was varied between 75 000 h⁻¹ and 110 000 h⁻¹ by manipulating the feed flow-rate. The targeted 90 % methane conversion was maintained by increasing the catalyst bed temperature as the catalyst deactivated during time on stream.

In order to investigate the effect of the presence of mine dust on the conversion of methane, a 1.0 wt% Pd/Al₂O₃ catalyst was mixed with mine dust and using the surrogate VAM feed described above, and the reaction carried out for more than 1200 h of continuous operation. The amount of mine dust mixed into the catalyst is estimated as the quantity of dust deposited for one year of operation (dust loading assumption of 2 mg·m⁻³).

Results and discussion

The activity of catalyst under dry and wet feed

The activity of 1.2 wt% Pd/Al₂O₃ catalyst was measured in alternating dry and wet conditions at a space velocity of 200 000 h⁻¹ as shown in Fig. 1. A shift in the T_{90} temperatures (which is a measure of activity) to higher values is observed with a humid compared to a dry feed VAM gas. Four alternating cycles of reactions were performed over the same catalyst, highlighting the deactivation phenomena. For the first cycle under a dry feed, complete combustion of methane was obtained at 380 °C. The addition of approximately 3.2 vol% water vapour into the VAM feed slightly reduces the activity of the catalyst within the second cycle experiment. When feed was switched back to dry (cycle-3), the conversion curve overlaps with the 2nd cycle, highlighting the loss of activity under wet feed conditions. Significant deactivation is revealed in the next wet cycle condition (cycle-4) where complete methane combustion was achieved at temperatures in excess of 470 °C.

Fig. 2 shows the time on stream behaviour of 1.2 wt% Pd/Al₂O₃ at 320 °C under dry and wet conditions for 12 h. Combustion of 8000 ppm of methane in dry air was changed to a wet feed (8000 ppm CH₄, 40 000 ppm H₂O balance air) after 2 h reaction. Once the wet feed was introduced, a sharp decrease in conversion is observed (from ca. 90 % to 40 % conversion). The activity quickly returns to the initial value when the water vapour in the feed is turned off, suggestive of reversible deactivation phenomena occurring, at least within 2 h oxidation under wet feed condition.

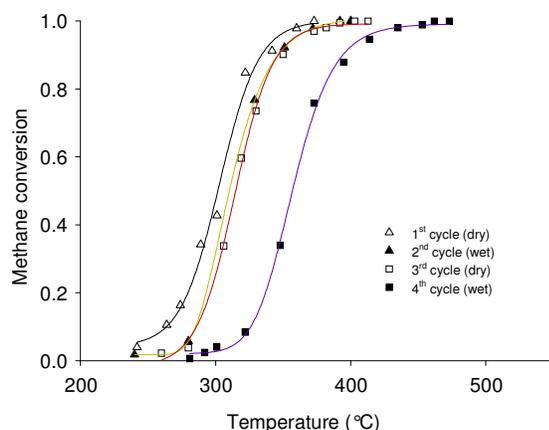


Fig. 1 Methane conversion as a function of reaction temperature of methane oxidation over 1.2 wt% Pd/Al₂O₃ catalyst using dry and wet feed. GHSV = 200 000 h⁻¹, CH₄ inlet = 8000 ppm, wet feed water vapour = 3.2 %.

Repeating the jump experiments up to 12 h does not disclose significant loss in activity over a relatively short time period. This behaviour suggests a competition for sites between water and methane^{11, 18} occurring in this period. Over this relatively short time period we suggest that, species described as responsible for catalyst deactivation such as Pd(OH)₂ are absent, which is supported by our XPS findings (see below).

Our findings are consistent with the results published by others, especially the pulse experiments as reported previously over palladium catalysts^{10, 11, 19, 20} under different reaction conditions. Over 4 % Pd/Al₂O₃ catalyst, Burch et al.¹⁰ observed reversible deactivation (an instantaneous drop from 40 % to nearly 10 % conversion at 325 °C) in catalytic activity. Likewise when 2.7 % of H₂O was added to a 1 % methane in air feed stream, other researchers concluded that, the formation of Pd(OH)₂ may not be important since palladium hydroxide under these conditions decomposes at the much lower temperature of approximately 250 °C.²¹ Roth and co-workers¹¹ also observed catalyst deactivation when exposed to a humid feed stream, with a slow initial deactivation stage followed by a dramatic drop in catalyst activity. The same authors suggested that, deactivation as a result of feed water vapour is reversible, while water produced in the reaction was suggested to cause irreversible catalyst deactivation. This was concluded from time-on-stream experiments for 6 h and 22 h runs respectively at 350 °C over 1.9 wt% Pd/Al₂O₃ (1 % of H₂O was added to 1 % CH₄, 4 % O₂, balance N₂).¹¹ It was suggested that, a progressive transformation of the active phase into less active phase occurred when water is present as a product.¹¹ In contrast to what can be presented in Fig. 2, within 2 h the activity is fairly constant. This is most likely a result of the exposure time of the active Pd sites with wet feed being insufficient to transform PdO into Pd(OH)₂, therefore we do not observe any irreversible deactivation. It also might be because of the high space velocity we used in our experiment, the transformation rate of active sites into less active sites is slowed compared to what has been reported by Roth and co-workers.¹¹

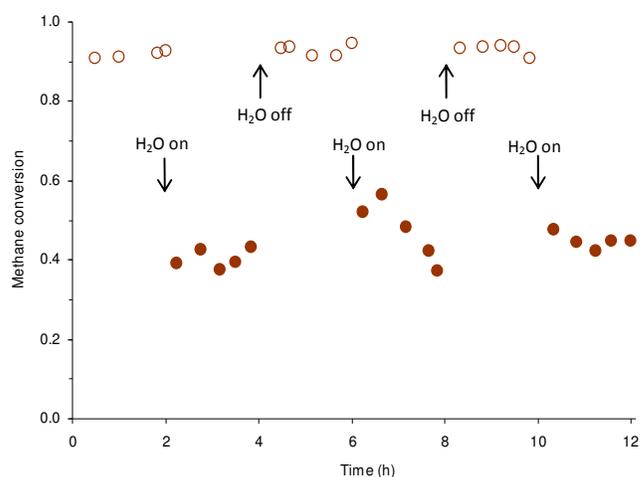


Fig. 2 Time-on-stream evolutions under dry and wet feed over 1.2 wt% Pd/Al₂O₃ catalyst at temperature of 320 °C. GHSV = 100 000 h⁻¹, CH₄ inlet = 8000 ppm, wet feed water vapour = 3.2 %. ○ = dry feed, ● = wet feed.

Stability evaluation of Pd/Al₂O₃ catalyst

In order to understand the reasons for catalyst deactivation over long periods on stream, a 1.0 wt% Pd/Al₂O₃ catalyst was operated continuously for 1150 hours. Prior to stability test, the activity of this catalyst has been tested and showed similar activities compared with 1.2 wt% Pd/Al₂O₃ catalyst (see Fig. S1 of supplementary information). The feed composition was 7000 ppm CH₄, 10 000 ppm CO₂, 30 000 ppm H₂O balance air where GHSV was in the range of 75 000 h⁻¹ – 110 000 h⁻¹. During the course of these experiments, the furnace temperature was periodically increased, in order to ensure that a conversion level of methane (in excess of 90 %) was achieved, mimicking the performance requirements for a large scale catalytic VAM mitigation system.

Fig. 3 shows the methane conversion as a function of reaction temperature for the system over this experimental period. The initial temperature of the system to achieve 90 % conversion was 350 °C, with this temperature increasing to 500 °C at a time of 1150 h. A significant rate of deactivation was observed during the first 80 h of reaction. In order to obtain high conversions, the bed temperature was increased from 320 °C to 420 °C during this period, ensuring the targeted 90 % conversion level of methane was re-established. The conversion level within the first 200 h of operation exhibits significant variation in activity. This is thought to be due to the initial deactivation phase of the catalyst, which appears to be comparatively fast. This result is detailed further in the ordinate which shows the catalyst bed temperature required to achieve 90 % methane combustion conversion. Please note that reoccurring of sharp drop in methane conversion is a result of a longer interval in bed temperature adjustment. The minor fluctuation in methane conversion level observed at nearly-fixed temperature of the furnace is mainly due the change in water vapour concentration which caused by changing in ambient temperature.

Following an initial deactivation period of the catalyst, methane conversion was maintained at 90 %, however it can be seen that after approximately 950 h, the conversion decreases to approximately 70 %. At this stage of the time-on-stream experiment, the GHSV was slowly reduced from 100 000 h⁻¹ to 75 000 h⁻¹ whilst maintaining the system temperature.

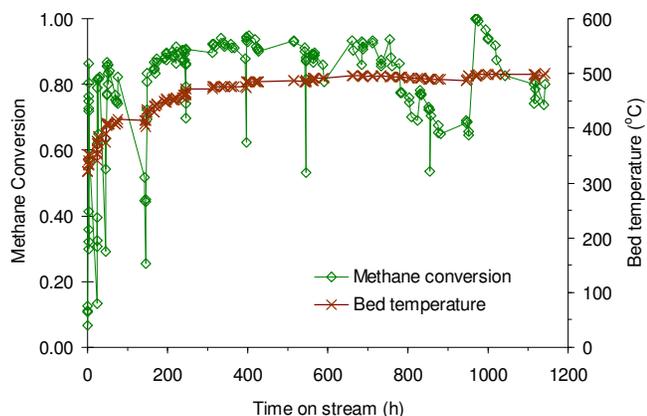


Fig. 3 Time-on-stream fractional methane conversion and corresponding reactor bed temperature over 1.0 wt% Pd/Al₂O₃ catalyst. Feed = 7000 ppm CH₄, 10 000 ppm CO₂, 30 000 – 40 000 ppm H₂O balance air. GHSV = 75000 – 110 000 h⁻¹. ◊ = methane conversion, × = bed temperature.

This was done in an attempt to maintain the targeted 90 % methane conversion without having to further increase the catalyst temperature. This test, however, did not have a significant effect on methane conversion. The GHSV was then increased to 110 000 h⁻¹ and the catalyst bed temperature increased to return the system to 90 % methane conversion. The catalyst bed temperature tends to plateau in the final stages of the run, suggesting that for long term use a constant temperature can be used to obtain stable conversion.

In order to investigate the long term effect of water produced from reaction, a VAM experiment under dry feed conditions was carried out for 1600 h where the reactant was 7000 ppm methane balance air at space velocity of 100 000 h⁻¹. The variation of the T_{90} temperatures is compared to VAM in a wet feed stream in Fig. 4. Similar to the conversion of a wet VAM feed stream, the temperature required to achieve in excess of 90 % conversion of CH₄ (T_{90}) increased over the duration of the experiment. Under wet feed conditions, the experiment was run continuously for a total of 1150 h with a catalyst bed temperature of 500 °C required to achieve 90 % methane conversion, while the dry VAM gas feed experiment was run for a total of 1610 h with a final catalyst bed temperature of 450 °C required for T_{90} . To estimate the conversion of methane and in order to assess the influence of the different conditions for the long term, the data for both the dry and wet run were extrapolated. Empirically, a logarithmic function was found to yield the best fit for the experimental data. The estimation results in a final bed temperature of 555 °C for the wet feed and 500 °C for the dry feed over a period of duration of 8760 h (1 year).

The effect of coal mine ventilation air dust on the conversion of methane was assessed and a wet VAM stream was operated continuously for over 7 weeks, where 60.8 mg VAM dust was packed in front of the 200 mg of catalyst. This quantity of VAM dust corresponds to the amount of dust deposited on the catalyst over a year of continuous operation. Time-on-stream variability, and reaction bed temperature over a 1.0 wt% Pd/Al₂O₃ catalyst, is shown in Fig. 5. The feed was 7000 ppm CH₄, 10 000 ppm CO₂, 32 000 ppm H₂O and balance air at space velocity of 100 000 h⁻¹. Significantly higher

fluctuations in the conversion levels and temperatures of the bed were observed in these experiments compared to the long term experiments in the absence of dust. One of the reasons for this fluctuation is likely to be a result of the combustion of coal particles present in the VAM dust and channelling with resulting changes in the pressure drop across the catalyst and dust beds (ca. 0.1 bar). After ca. 700 h on stream, it was noticed that there was a significant decrease in methane conversion. The bed temperature was continually increased to 550 °C over a period of 150 h (time on stream 950 h) in order to restore the conversion level to 90 %. As the conversion did not increase, it was suspected that the catalyst bed had shifted slightly, into a lower temperature zone of the furnace. The bed was then opened and it was confirmed that the catalyst bed had moved. After that, the catalyst was repacked and the experiment continued. Subsequent to repacking, the catalyst exhibited similar conversion levels observed before the bed movement. No difference in methane conversion and temperature were observed within the experimental error. This is an experimental artefact due to high volumes of VAM dust, which would not be present in a real VAM mitigation system.

Characterization of catalysts

The nitrogen adsorption isotherm experiment results in estimates of the Langmuir surface areas of 98.4 m²·g⁻¹, 92.8 m²·g⁻¹ and 193.4 m²·g⁻¹ for γ - δ -Al₂O₃, 1.2 wt% Pd/ γ - δ -Al₂O₃, and 1.0 wt% Pd/ γ -Al₂O₃ (commercial catalyst), respectively. Note that the alumina phase used for catalysts prepared in these experiments is somewhat different to what has been used for commercial catalysts, confirmed by our XRD results. The surface area of the commercial catalyst is somewhat higher, although the activity of the catalysts is similar. Thus, as expected, the support surface area appears to have very little influence on catalytic activity. ICP-OES confirms the loading of 1.0 and 1.2 wt% of Pd on their supports respectively.

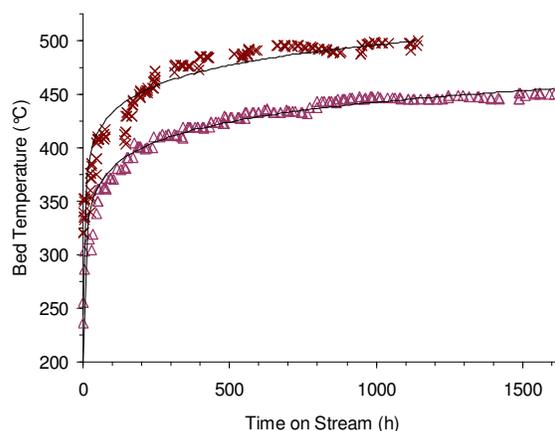


Fig. 4 Catalyst bed temperature required for 90 % CH₄ conversion for wet (30 000 – 40 000 ppm H₂O) and dry time on stream runs over 1.0 Pd/Al₂O₃ catalyst. Feed: 7000 ppm CH₄ balance air, GHSV = 100 000 h⁻¹. × = wet feed run; △ = dry feed run.

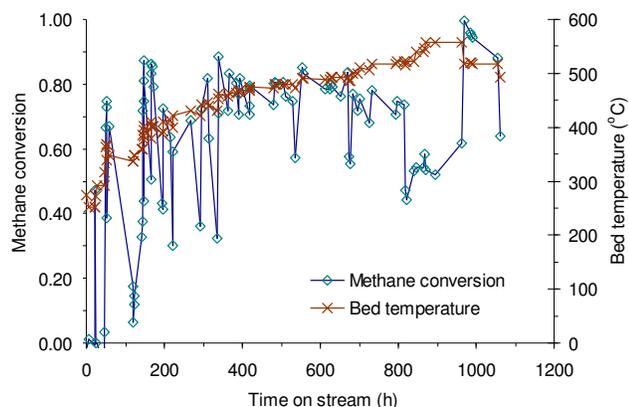


Fig. 5 Time-on-stream evolutions and reactor bed temperature over 1.0 wt% Pd/Al₂O₃ catalyst in the presence of VAM dust. Feed = 7000 ppm CH₄, 10 000 ppm CO₂, 32 000 ppm H₂O balanced air. GHSV = 100 000 h⁻¹. ◊ = methane conversion, × = bed temperature.

The XRD pattern of Pd/Al₂O₃ catalysts reveal minute reflections attributed to Pd or PdO phases (overlapping with support peaks, thus they were identified by slightly increased intensities and widths of support reflections), consistent with a low net metal loading and suggests small noble metal particles. The overlap with the support reflections and the small size makes particle size estimation from XRD difficult. As reported in our previous works, the particle size of the palladium was estimated from the results of pulse H₂-chemisorption at 109.1 °C showing that the average catalyst particle diameter is 12.2 nm, corresponding to a 9.2 % level of metal dispersion.²² This particle size estimation agrees with what has been observed with TEM analysis, where particle sizes were measured to vary between 6 and 13 nm.²²

The influence of water vapour adsorption on the active site and the support was investigated using TPD analysis. The intensity of water desorbed from the support material (γ - δ -Al₂O₃) and 1.2 wt% Pd/Al₂O₃ catalysts are plotted in Figure 6(a) for fresh active catalyst and 6(b) for the used catalyst (7 hours at 320 °C). Prior to water adsorption, fresh catalysts were pre-heated for 1 h at 500 °C with a ramp of 5 °C·min⁻¹ and H₂O adsorption was at 110 °C, while on Pd/Al₂O₃ (used catalyst) the water was adsorbed during combustion of methane with a wet feed at 320 °C for 7 h.

In all cases, high and low temperature desorption peaks can be observed. The low temperature peak is observed at ca 240 °C and the high temperature peak was observed between 350 °C and 700 °C. The low temperature desorption is attributed to

weakly bound water, whereas the high temperature peak is attributed to adsorption on coordinatively unsaturated sites.^{23, 24}

Over a fresh alumina surface (Figure 6a), a second desorption peak is observed at ca 600 °C. On fresh Pd-containing catalysts, the second temperature desorption peak of water was observed at higher temperatures than on the support, indicating that water is more strongly bound on the Pd-containing surface. The higher temperature peak (600 °C) observed for the support material shifts to 700 °C, which suggests either a change in the interaction strength of the sites or structural and chemical changes of the sites by Pd. We suggest that Pd is deposited on sites that can interact strongly with water and transforms into sites that bind even more strongly with water. A small quantity of water is retained on the catalyst at temperatures as high as 700 °C, similar to what was observed by Mowery and co-workers.¹² This further underscores the formation of catalyst sites interacting strongly with water.

Over the used catalyst (Figure 6b), the maximum water desorption rate was observed at ca 350 °C. A quantified amount of water remains on the catalyst at these temperatures (as indicated by the relative area under the peak), suggesting significant number of sites are interacting with water/form hydroxides. The desorption peak around 350 °C most likely is due to water desorption from hydroxides, consistent with the decomposition temperature of Pd(OH)₂.²¹ The high temperature peak at ca. 700 °C was not observed, suggesting the absence of sites that are able to strongly adsorb water. Highly coordinatively unsaturated sites could be crucial as site for oxygen activation and would result in deactivation of the catalyst, similar to what has been suggested in ⁸. These coordinatively unsaturated sites often are described as edge or corner or surface sites on metal and metal oxides.²⁵ Our estimation of the amount of water adsorbed during experiment is 0.9×10⁻³ mol·g⁻¹ and 1.1×10⁻³ mol·g⁻¹ for the support and the Pd/Al₂O₃ catalyst, respectively. The ratio of water desorbed from catalyst versus amount of Pd is 10, which means majority of water is adsorbed on the support. However, the presence of palladium on alumina increases the quantity of H₂O_(v) adsorbed and also results in significant water desorption peak shift toward higher temperatures. This suggests significant interaction of Pd with water.

XPS spectra of activated (calcined-reduced) and used 1.2 wt% Pd/Al₂O₃ catalyst are displayed in Fig. 7. The binding energies (BE) and Pd/Al ratios are provided in Table 1 for all samples.

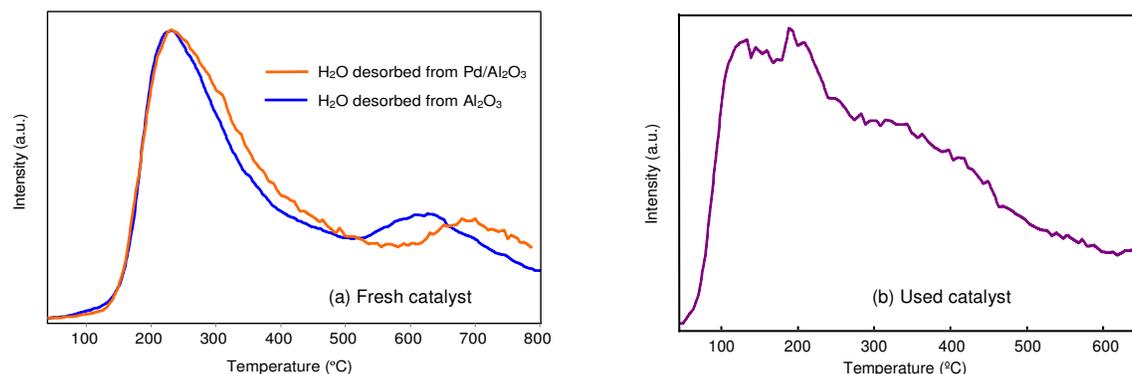


Fig. 6 TPD curves of water desorption from (a) fresh catalyst (1.2 wt% Pd/Al₂O₃) and catalyst support (γ - δ Al₂O₃) from and (b) used catalyst time on stream 7 h, Feed; 6000 ppm CH₄, ca. 30 000 ppm H₂O, reaction temperature 320 °C.

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Table 1. XPS peak positions and Pd/Al ratio

Fig.	Sample	Pd 3d _{5/2} peak position (eV)		Pd/Al ratio
		Pd ⁰	Pd ²⁺	
7a.	1.2 Pd/Al ₂ O ₃ , calcined-reduced	335.0	336.3	0.0046
7b.	1.2 Pd/Al ₂ O ₃ , 2 h usage	335.0	336.4	0.0040
7c.	1.2 Pd/Al ₂ O ₃ , 10 h usage	-	336.0 337.1	0.0077
8a.	1.0 Pd/Al ₂ O ₃ , fresh	334.7	336.1	0.0045
8b.	1.0 Pd/Al ₂ O ₃ , calcined-reduced	335.2	336.4	0.0045
8c.	1.0 Pd/Al ₂ O ₃ , 1150 h usage	-	336.3	0.0040
9a.	1.0 Pd/Al ₂ O ₃ , used in the presence of dust	-	335.9	0.0048
9b.	Dust contaminated with Pd/Al ₂ O ₃ , used	-	336.2	0.0018

XPS spectra of the activated and reduced 1.2 wt% Pd/Al₂O₃ catalyst (Fig. 7a), reveal two distinct Pd peaks representing the Pd 3d_{5/2} core level transitions. The palladium species at 335.0 eV and 336.3 eV can be attributed to Pd⁰ and Pd²⁺ respectively. These species are formed during catalyst activation under air and hydrogen. The presence of metallic Pd and PdO has been assigned, by comparison with shifts reported in the literature.^{3, 26, 27}

The XPS spectra of the 1.2 wt% Pd/Al₂O₃ catalyst used for 2 h under dry and wet feed at 335 °C are plotted in Fig. 7b. Two species with a binding energy (BE) of 335.0 eV and 336.4 eV were observed. The binding energies are similar to the BE obtained from the calcined-reduced sample (Fig. 7a) which suggests little change in the chemical nature of Pd⁰ and Pd²⁺. This observation supports our experimental data presented in Fig. 2 where the loss of activity 2 h under wet stream is completely reversible and no structural or chemical changes in the catalyst were detected.

Following reaction with lean air-methane mixtures at a temperature of 290 °C for 10 h, the 1.2 wt% Pd/Al₂O₃ catalyst was deactivated and the XPS spectra of this sample is shown in Fig. 7c. The shape and width of the peak (FWHM = 2.3 eV at Pd 3d_{5/2} line) suggests the presence of multiple palladium species. Similar to the spectra of the fresh sample, asymmetry toward higher binding energies indicates that multiple peaks should be fitted. Assuming Gaussian-Lorentzian curves (70 % Gaussian), the peak fitting results in two different photoelectron energies at BE of 336.0 eV and 337.1 eV (3d_{5/2} core level). Adding additional peaks results in little improvements in the Chi² fit and is thus statistically not significant. The lower energy peak at BE of 336.0 eV is identified as bulk Pd²⁺ as

reported in the literature.^{3, 27} The presence of PdO corresponds to Pd species identified in Fig. 7a, which indicates transformation of Pd metal into the oxidized form under reaction conditions. The signal at a higher BE of 337.1 eV can be interpreted as palladium hydroxide (*vide infra*), which appears to be related to the deactivation observed during time on stream.

A limited body of research describing hydroxyl compounds was identified, and correlations between progressive alterations in chemical bonding and shifts in XPS binding energies with the nature of hydrogen bonding have been proposed.²⁸ A change in the binding energy of Pd(OH)₂ was reported by Barr²⁹ when a hydroxide layer is present on the palladium surface. Experimentally, Barr found that the Pd⁰ peak at a BE of 335.4 eV was shifted to 336.9 eV and 338.6 eV upon formation of PdO and Pd(OH)₄, respectively.^{28, 29} These shifts in binding energies are similar to what has been observed for Pd 3d_{5/2} in our samples (see Fig. 7). The presence of O-H groups on palladium metal can result in a shift of the peak of 1.1 eV toward a higher binding energy. The formation of palladium hydroxide is further substantiated by the regeneration of the active sites when a deactivated catalyst was heated in He (15 ml·min⁻¹) at 500 °C for 1 h. H₂ was detected in the exit stream, which most likely originates from OH groups on the catalyst surface. The TPD spectra plotted in Figure 6 also support the argument of palladium hydroxide being present in the deactivated sample and are responsible for deactivation.

The spectra of a fresh, activated and used samples of 1.0 wt% Pd/Al₂O₃ catalyst in the Pd 3d core level region are shown in Fig. 8. For the fresh (as received, Fig. 8a) and activated (calcined-reduced, Fig. 8b) samples, the peak deconvolution results in two species detected at Pd 3d_{5/2} core level. These species are having similar binding energies as reported in Fig. 7a and 7b.

Figure 8c shows the spectra of used 1.0 wt% Pd/Al₂O₃ catalyst after 1150 h operation using a surrogate VAM gas (refer to catalyst activity data plotted in Figure 3). XPS analysis of the catalyst discloses a single peak of Pd 3d_{5/2} core level at 336.3 eV. The presence of a single Pd²⁺ species is proposed as the full width at half maximum of Pd 3d_{5/2} is only 1.8 eV, which is indicative of a single species. Fitting more peaks under Pd 3d spectra, does not significantly decrease Chi².

XPS spectra in figure 8c suggest no palladium hydroxide is present on the catalyst. The increased bed temperature leads to decomposition of hydroxyl species, resulting in a single peak which is interpreted as PdO species dispersed on the support. An increase in Pd crystallite size is suggested to be an important contributor for deactivation as formation of Pd(OH)₂ was not found most likely due to the higher temperature.

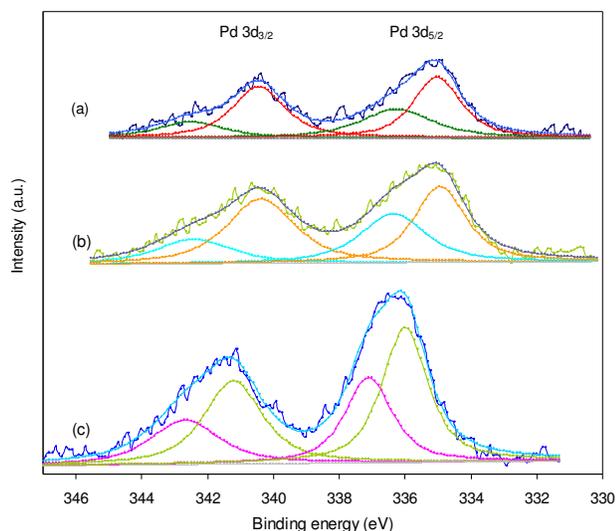


Fig. 7 XPS spectra of Pd 3d core level of 1.2 wt% Pd/Al₂O₃, (a) calcined-reduced sample; (b) used sample of 2 h TOS under humid condition; (c) used sample of 10 h TOS under humid condition.

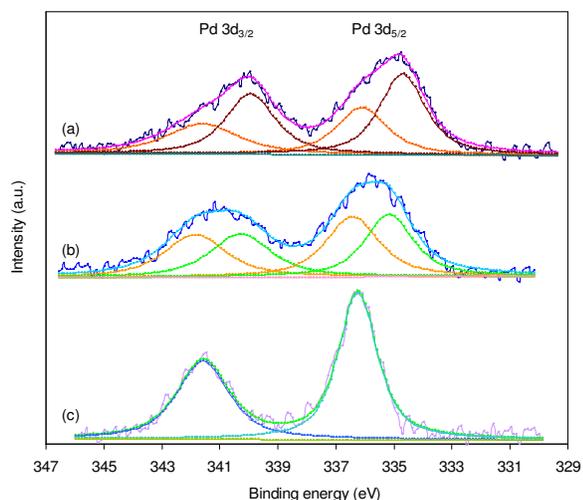


Fig. 8 XPS spectra of Pd 3d core level of 1.0 wt% Pd/Al₂O₃, (a) fresh sample; (b) calcined-reduced sample; (c) used sample of 1150 h stability test.

The accumulation of H₂O on the catalyst increases the surface mobility and results in particle agglomeration as well as potentially hinders the oxygen transfer from the bulk in a Mars van Krevelen type reaction mechanism.⁸ As suggested by Lee and Trimm, thermal deactivation is caused by either sintering of the catalyst or support material.³⁰ This sintering involves surface/volume diffusion and other transformations. At reaction temperatures close to $0.3 \times$ melting point (Hüttig temperature), the transformation becomes significant.³¹ In our study, after ca. 300 h, the bed temperatures were adjusted toward 500 °C close to the Hüttig temperature for Pd at 466 °C, and thus, a significant level of sintering would be expected. Please note that the binding energy of the Pd²⁺ of catalyst used in humid conditions for 1150 h slightly decreases compared to the fresh

samples, similar to the catalyst aged in the presence of VAM dust. This is consistent with sintering (see below).

The used 1.0 wt% Pd/Al₂O₃ catalyst from VAM-dust time on stream experiment was analyzed by XPS in order to determine the surface composition of catalyst and dust after 1100 h operation. Fig. 9 shows the palladium 3d photoelectron spectra of used catalyst (a) and used dust mixed with catalyst (b). The binding energies compiled along with Pd/Al atomic ratio are provided in Table 1. Deconvolution of the peak at Pd 3d_{5/2} core level suggests a single peak at a binding energy of 335.9 eV for the used catalyst. This peak is identified as Pd²⁺, which is similar species detected from samples in Fig. 7 and Fig. 8, and is in agreement with the previous discussion suggesting palladium oxide is the primary species present on the surface after long term time on stream experiment. Note the decreased binding energy of the used sample (9a) compared to the activated sample (8b). The decreased binding energy can originate from chemical shift but also final state effects due to relaxation of the core hole. For larger particles, this relaxation effect is less important compared to smaller particles. Thus, the shift can be evidence for larger particles in the used samples, i.e., sintering. Despite a lower intensity, an identical peak is detected also from the XPS spectra of used dust at similar binding energies. As suggested by the overall surface composition of the used catalyst in Table 2, impurities such as Na, Cl and F were also present. It is important to note that the deactivation was little affected by the presence of the VAM dust and these species play a minor role in deactivation.

From the used catalyst, XPS evidence disclosed that ca. 0.24 % of chlorine deposited on used catalyst while chlorine was not detected in the fresh catalyst and used dust (see Table 2). Others have suggested that chlorine ions behaves as a powerful inhibitor during methane oxidation over supported Pd catalyst^{11, 32, 33} and removing the chlorine from the surface takes a minimum 10 h reaction even at temperatures as high as 600 °C.¹¹

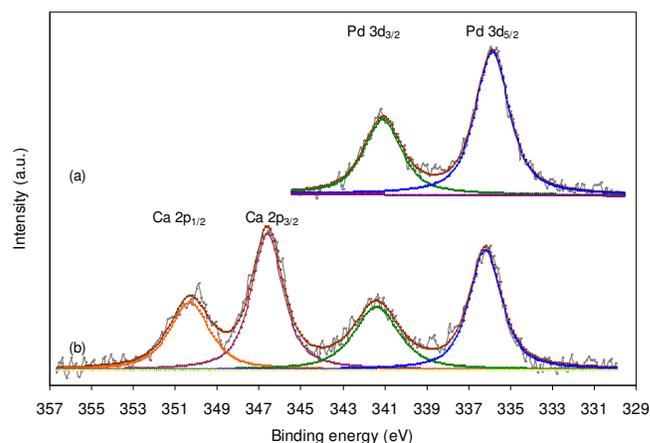


Fig. 9 XPS spectra of Pd 3d core level of used 1.0 wt% Pd/Al₂O₃ catalyst in the presence of dust, (a) used catalyst; (b) used dust mixed with catalyst.

Table 2. Surface composition of used catalyst and a mixture of VAM dust and used catalyst.

Sample	Composition (at.%)													
	Pd	O	Al	C	Na	N	Cl	F	Si	Mg	Ca	S	Fe	
(a) Used Pd/Al ₂ O ₃ (in the presence of dust)	0.18	57.9	37.2	3.85	0.15	0.22	0.24	0.29	-	-	-	-	-	
(b) Used Dust+ Pd/Al ₂ O ₃ contamination	0.09	43.3	49.1	4.48	0.45	0.33	-	0.22	0.99	0.31	0.44	0.33	-	
(c) VAM dust (fresh)	-	39.4	3.2	34.0	0.8	1.4	3.5	-	6.0	5.1	6.2	-	0.4	

Since our reaction temperature is below 550 °C, it appears that chlorine remains on the surface of the catalyst and inhibits catalytic activity. As can be seen in Figure 5 over 1100 h reaction, an increase in bed temperature can increase methane conversion. However, it is important to note that in maintaining an average methane conversion > 75 % over 1100 h our reaction temperature does not exceed 600 °C.

Characterization of the VAM dust

The XRD trace of VAM dust (Fig. S2 of SI) following long term catalytic reaction discloses the presence of calcium carbonate, quartz and iron oxide as distinct phases. Consistent with the phase analysis by XRD, elemental analysis reveals the presence of Ca, Fe and Si (see Table 2). In addition aluminium, magnesium and titanium were also detected in the samples. These elements may be present as amorphous silicates. Surface analysis by XPS resulted in similar composition as determined by ICP-OES.

XPS analysis of the used catalyst and dust reveals the presence of chlorine on the catalyst. Chlorine can have a significant effect on the activity of the noble metal catalysts and has been detected in the catalyst after 1200 h of reaction. As indicated in Table 2, XPS of the separated VAM-dust revealed that chloride was likely removed from VAM gas and deposited on the catalyst surface. Note that complete separation of dust and catalyst was not possible. The presence of Cl in the XPS (Table 2) and its absence in ICP-OES suggests surface enrichment of chlorine on the catalyst that was operating in the presence of VAM dust. As already noted, the VAM dust influenced the overall activity (T_{90} at 1100 h was 550 °C compared to experiment without dust $T_{90} = 500$ °C) but the deactivation was not dramatic. Thus, chlorine does have some but not a significant impact on the deactivation under our conditions.

Conclusions

The stability of a palladium supported on alumina has been evaluated during short and long term experiments in the presence of water and VAM dust. Within 2 h during, alternating experiments in dry and wet VAM feed suggests ca. 50 % reversible drop in activity, most likely due to competition between water and methane to adsorb on the active sites. For short term VAM oxidation, palladium hydroxide was not detected. Prolonged exposure to water leads to formation of palladium hydroxide and progressively deactivates Pd/Al₂O₃ catalyst. A long term stability test with humid synthetic ventilation air methane reveals that 90 % conversion can be

achieved for a period of 1150 h at temperatures ≤ 500 °C. The water vapour present in the feed stream is the primary factor responsible for catalyst deactivation. Introducing VAM dust into reactor lead to some reduced activity most likely due to an inhibition effect of chloride ions on the surface of catalyst. Nevertheless, in the presence of ventilation air dust an average methane conversion higher than 75 % can be achieved over 1100 h at a reaction temperature below 600 °C.

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Notes

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† Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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This paper presents long-term evaluation of catalyst stability and durability in the presence of water and coal mine dust.

