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# Stability of palladium-based catalysts during catalytic combustion of methane: The influence of water

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## Abstract

The stability of methane conversion was studied over a Pd/$Al_2O_3$ catalyst and bimetallic Pd–Pt/$Al_2O_3$ catalysts. The activity of methane combustion over Pd/$Al_2O_3$ gradually decreased with time, whereas the methane conversion over bimetallic Pd–Pt catalysts was significantly more stable. The differences in combustion behavior were further investigated by activity tests where additional water vapor was periodically added to the feed stream. From these tests it was concluded that water speeds up the degradation process of the Pd/$Al_2O_3$ catalyst, whereas the catalyst containing Pt was not affected to the same extent. DRIFTS studies in a mixture of oxygen and methane revealed that both catalysts produce surface hydroxyls during combustion, although the steady state concentration on the pure Pd catalyst is higher for a fixed temperature and water partial pressure. The structure of the bimetallic catalyst grains with a PdO domain and a Pd–Pt alloy domain may be the reason for the higher stability, as the PdO domain appears to be more affected by the water generated in the combustion reaction than the alloy. Not all fuels that produce water during combustion will have stability issues. It appears that less strong binding in the fuel molecule will compensate for the degradation.

*Keywords:* Palladium; Platinum; Bimetal; Methane; Catalytic combustion; Stability; Water; DRIFTS

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## 1. Introduction

Catalytic combustion of methane has attracted attention both in the field of emission control [1,2] and power generation in gas turbines [3]. Methane is an undesirable emission from natural gas-powered vehicles due to its high global warming potential. Emissions of methane could be decreased using catalytic exhaust converters. Catalytically stabilized combustion can also be used in gas turbine combustors. This combustion technique is attractive because it offers the potential of ultra-low $NO_x$ levels, which is difficult to achieve with other conventional techniques. Since stationary gas turbines most often are powered by natural gas, degree of methane conversion becomes essential.

Palladium catalysts are renowned for their high activity in methane combustion and have been studied a great deal over the years [4–6]. However, the drawback with these catalysts is their poor stability, resulting in severely decreasing activity during operation [7–12]. No clear consensus regarding the cause for the deactivation has been reached in the literature. Narui et al. [8] have explained the poor stability by sintering of the PdO particles during operation. However, this explanation has been rejected by others that have shown that dispersion does not change considerably upon aging [13]. The reason for the loss in conversion has also been attributed to inhibition from the water generated during the oxidation process [14–20]. The cause of the water inhibition is suggested to be inactive hydroxyls groups being formed on the catalysts surface, which block access to the PdO sites for methane dissociation. Therefore, if water inhibition is the cause for deactivation, it is important to find a way to improve the water resistance of the palladium catalyst.

Several studies have shown that the stability of conversion is considerably improved by adding platinum to the supported palladium catalysts [8–12,21]. This is confirmed both for longer durations and at higher pressures [12,22]. Even though water inhibition may be the reason for deactivation of monometallic catalysts, few studies have investigated how the water affects

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bimetallic Pd–Pt catalysts. In the present study, both Pd and bimetallic Pd–Pt catalysts have been investigated by means of different activity tests and DRIFTS measurements in order to explain the water effect.

## 2. Experimental

### 2.1. Catalyst preparation

A monometallic palladium catalyst and two palladium–platinum catalysts were prepared for this study. Alumina powder ($\gamma$-$Al_2O_3$, PURALOX HP-14/150, Sasol Germany GmbH) was impregnated with the metal/metals using the incipient wetness technique. The bimetallic catalysts were prepared by co-impregnation of the two metals, by mixing solutions of palladium and platinum nitrate. The support was impregnated twice, with a drying step at 300 °C for 4 h in between, and calcined at 1000 °C for 1 h. All catalysts had a loading of 470 μmol metal/g catalyst powder. The details regarding these catalysts are summarized in Table 1.

The catalyst powders were suspended in ethanol and ball-milled for 24 h prior to coating the monoliths. Cordierite monoliths (400 cpsi, Corning), with $\phi$ 14 mm and length 10 mm, were then dipped into the slurry followed by a drying step at 100 °C. This procedure was repeated until 20 wt.% of catalyst material was fastened onto the monolith. Finally, the coated monoliths were calcined at 1000 °C for 2 h.

### 2.2. Characterization

Inductive coupled plasma-atomic emission spectroscopy (ICP-AES) was performed on all catalyst powders in order to verify the amounts of palladium and platinum.

The specific surface areas of the catalyst powders were measured according to the Brunauer–Emmett–Teller (BET) theory by nitrogen adsorption at the liquid $N_2$ temperature in a Micromeritics ASAP 2010 instrument. Prior to analysis, the samples were degassed for at least 2 h at 250 °C.

The CO-chemisorption measurements were performed on the catalyst powder by using a volumetric technique. Prior to the measurements, the samples were dried in vacuum at 120 °C, reduced in a flow of $H_2$ at 300 °C for 1 h, evacuated at 300 °C for 1 h and then cooled to 35 °C. The CO-chemisorption analyses were thereafter carried out using a dual isotherm method.

The crystal phases in the various catalysts were identified by means of powder X-ray diffraction (PXRD) using a Siemens Diffraktometer D5000. The operation parameters were: Cu K$\alpha$ radiation, Ni filter, 30 mA, 40 kV, step size 0.02 and 2$\theta$ scanning from 20 to 80° at a rate of 1 s per step. The crystal phases of the noble metals were studied more carefully in between 32 and 44°, by a step size of 0.01 at a rate of 8 s per step. Phase identification was done using the reference JCPD database and the mean crystal size estimation was done using the Fundamental Parameter Approach application of the *TOPAS v2.0* software.

The DRIFTS spectra were recorded using a Nexus 870 FTIR instrument equipped with a diffuse reflectance accessory that includes a reaction cell. The catalyst powder was placed inside the reaction cell, in which the temperature and atmosphere were controlled. The spectrometer collected 42 spectra in the range of 2000–4000 $cm^{-1}$, with a resolution of 16 $cm^{-1}$ at a mirror velocity of 1.89 cm $s^{-1}$.

A typical run consisted of several steps. In order to remove absorbates from the catalyst surface, the powders were pretreated in 4% $O_2$/He flowing at 35 ml/min; the temperature was elevated to 320 °C and kept constant for 1 h. After cooling to the desirable reaction temperature, a background was collected using the parameters for the spectra collection described above. Thereafter, the programmed collection of series of spectra started simultaneously with a gas tank mixture of 1% $CH_4$, 4% $O_2$, balance He being switched on. It was added to the feed into the reaction cell. The collection lasted for 50 min, while the temperature was kept constant. In order to study the desorption of species, the methane flow was turned off after 30 min.

### 2.3. Activity measurements

The measurements of the catalytic activity of the different catalysts were carried out in a tubular reactor, equipped with a temperature-programmed furnace. The temperature was recorded in the gas phase by a thermocouple placed upstream of the monolith. The gas compositions used in the experiments consisted of 1.5 vol.% fuel in air, where the fuel was methane in most cases, but also hydrogen and ethane have been tested.

The first experiment was carried out at a gas hourly space velocity of 250 000 $h^{-1}$. For this experiment the composition of the product gas was analyzed by gas chromatography, using a Varian 3800 instrument equipped with a thermal detector. The activity of methane combustion was measured for 12 h, when the temperature was maintained at 500 °C.

The following activity tests were carried out at a gas hourly space velocity of 100 000 $h^{-1}$ and the composition of the

Table 1
The nomenclature, the metal loading, the BET surface area, CO uptake and the crystal size of the three catalysts

| Sample | $Pd/Al_2O_3$ | $2{:}1PdPt/Al_2O_3$ | $1{:}1PdPt/Al_2O_3$ |
|---|---|---|---|
| Composition | 5 wt.% $Pd/Al_2O_3$ | 2:1 Pd:$Pt/Al_2O_3$ | 1:1 Pd:$Pt/Al_2O_3$ |
| Pd loading (wt. %) | 5.01 | 3.3 | 2.6 |
| Pt loading (wt. %) | – | 3.0 | 4.7 |
| BET surface area ($m^2$/g) | 102 | 91 | 107 |
| CO-uptake (μmol/g catalyst) | 7.3 | 5.2 | 7.0 |
| Crystal size PdO (nm) | 27 | 22 | 23 |
| Crystal size Pd–Pt (nm) | – | 47 | 36 |