



Influence of gas composition on activity and durability of bimetallic Pd-Pt/Al₂O₃ catalysts for total oxidation of methane



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ABSTRACT

The total oxidation of methane was studied over a Pd-Pt/Al₂O₃ catalyst with selected variations of typical gaseous emission components of natural gas engines being oxygen, methane, water, carbon dioxide, higher hydrocarbons, CO, NO_x, and SO₂. The light-off, durability and reactivation of deactivated samples were studied. A continuous deactivation of the catalyst was observed in methane/air. In situ XAS revealed a Pd oxidation state +2 under these conditions. No pronounced changes in BET surface area, noble metal dispersion, and oxidation state were observed for the deactivated samples. However, the deactivation is accompanied by segregation of Pt and Pd in core-shell bimetallic particles. This deactivation did not occur in the presence of NO_x. The catalyst could furthermore be reactivated in the presence of NO_x as well as by the reduction in hydrogen. Even a small addition of SO₂ was observed to have a pronounced negative impact on the catalyst activity and durability. This deactivation is attributed to the blocking of active noble metal sites by sulfur compounds, because the number of active sites is drastically reduced as observed by CO-chemisorption measurements.

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1. Introduction

Lean burn gas engines presently become more attractive since they are able to use gases from various sources such as natural gas, biogas, and synthetic methane (Power-To-Gas). Additionally, gas engines provide high efficiency while emitting little particulate matter (PM) and NO_x. This advantage can be attributed to a high H/C ratio in the gaseous fuel, homogenous combustion, and low combustion temperature. However, gas engines suffer from methane slip, i.e. the release of a small amount of unburned methane into the exhaust. Methane, the main component of the gaseous fuel used, is a strong greenhouse gas (~20 times stronger than CO₂). Therefore emission regulations are becoming stricter making the removal of unburned methane crucial for future operation of gas engines in both transport (natural gas vehicles (NGV), trucks and ships) and stationary applications (power plants).

Among alkanes, methane is the kinetically least reactive molecule [1–3]. In this respect, Pd based catalysts are generally

considered to be the most active catalysts for total oxidation of methane under lean conditions [4,5]. Although the reaction has been studied over several decades, mechanistic details and the identification of the most active oxidation state are still discussed. PdO seems to play an important role in the complete oxidation of methane. Furthermore, a reduction to metallic Pd at high temperature was found to lead to lower activity [6,7]. However, several studies revealed that Pd catalysts reduced prior to the methane oxidation reaction are more active than completely oxidized Pd catalysts, i.e. PdO [8–10]. Hellman et al. concluded from DFT-calculations supported by in situ X-ray diffraction that under-coordinated Pd in PdO has the lowest activation energy for the dissociative adsorption of methane, which is considered to be the rate determining step [11]. Furthermore, it could recently be shown that methane oxidation activity depends on noble metal particle size under lean conditions [9,12,13]. The turnover frequency (TOF) increases with increasing Pd particle size in the range of 1–20 nm as reported by Stakheev et al. [14].

Another important aspect is the impact of the gas composition on the activity and especially on durability of Pd catalysts. Bugosh et al. [15] reported a strong dependency of methane conversion on O₂ concentration of a Pd-Pt-catalyst especially around the stoichiometric point, which is dependent on the history of the catalyst. Particular focus was also laid on the influence of water

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[16–20] which typically exhibits a negative effect. Probably, this is due to the formation of surface hydroxyls on the Pd-particle surface or on the support, which hinders oxygen exchange between support and active sites. This process was also observed to lead to a deactivation during long-term usage [21]. However, experiments performed by Escandon et al. [19] showed that deactivation with wet feeds was reversible and the investigated Pd/ZrO₂ catalyst could be reactivated by dry feeds for a certain time. Also sulfur compounds, typically present in very low concentrations, have been reported to have a distinct negative effect on the catalyst activity and on its durability [22–25]. Poisoning of active sites, caused by the formation of sulfates or sulfites [23] hinders the catalytic reaction and required reactivation by heating to elevated temperatures [26,27].

To overcome some of the drawbacks of Pd catalysts, several studies aimed at optimizing the support to gain a higher activity and durability [28,29], e.g., to enhance the sulfur resistance [30]. Furthermore, the addition of small amounts of Pt was reported to increase the low temperature activity [31], especially under wet feed conditions, and also to improve the thermal durability [32–34]. However, the reason leading to the positive effect of small amounts of Pt is still strongly debated.

The main goal of the present study is the systematic investigation of the influence of various gases typically present in gas engine exhaust on the long-term activity of Pd-Pt/ γ -Al₂O₃ catalysts. Furthermore, complementary characterization methods such as CO-chemisorption, N₂-physisorption, X-ray diffraction (XRD), X-ray absorption spectroscopy (XAS), and high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) are used to identify the structural and morphological changes being responsible for the deactivation of the catalyst.

2. Experimental

2.1. Catalyst

For this study, a commercial Pd-Pt model catalyst provided by Heraeus, a technology group headquartered in Hanau, Germany, was used. The washcoat, consisting of Pd and Pt in a weight ratio of 5 to 1 on γ -Al₂O₃, was deposited (100 g/ft³) on a cordierite honeycomb with 400 cpsi. For activity measurements, cylindrical cores of the honeycomb structure of 5 and 2 cm length and a diameter of 2.54 cm were used. For characterization, either the catalyst powder (XAS and STEM measurements), the scraped-off catalyst layer (N₂-physisorption, XRD, STEM, XAS measurements) or the monolithic samples (CO-chemisorption) have been employed.

2.2. Catalyst characterization

The specific surface area was measured using N₂-physisorption at 77 K on a Rubotherm Belsorp-mini II instrument using the Brunauer–Emmet–Teller (BET) method. Prior to the measurements, all samples were degassed at 573 K for 2 h under vacuum.

Powder X-ray diffraction (XRD) patterns were recorded with a PANalytical X'Pert Pro powder diffractometer in a 2θ range of 20–80° (2 steps s⁻¹, with an angular step interval of 0.017°) using Cu K α radiation ($\lambda = 1.54 \text{ \AA}$).

The morphology of the catalyst was studied by HAADF-STEM on an aberration-corrected FEI Titan³ 80-300 transmission electron microscope at 300 kV acceleration tension. The chemical composition of single nanoparticles was investigated by energy-dispersive X-ray spectroscopy (EDXS) performed with the FEI Titan³ 80-300 microscope at 300 kV by using an EDAX Si(Li) detector. EDX spectra are quantified with the FEI software package “TEM imaging and analysis” (TIA) version 3.2. Using TIA, element concentrations

were calculated on the basis of a refined Kramers' law model, which includes corrections for detector absorption and background subtraction. EDX spectra obtained during scanning of a rectangular area within single nanoparticles are used to determine their average chemical composition. The concentration profiles of different chemical elements within a nanoparticle were determined from EDX spectra measured along a line-scan that passes through its center. EDX profile analysis and determination of complex nanoparticle compositions was performed as described in detail in ref. [35]. In case of Pd-Pt nanoparticles the quantification of EDX spectra (area or line-scans) is performed on the basis of the characteristic X-ray lines. Samples for HAADF-STEM were prepared by deposition of particles on an amorphous carbon (Lacey-)film copper grid.

The overall noble metal dispersion was determined using temperature programmed desorption of CO (CO-TPD) under continuous flow (0.5 L/min flow at standard ambient temperature and pressure (SATP)) [36]. The monolithic samples were placed in a tubular quartz glass flow reactor and fiber glass insulation was used to avoid bypass of gases. Prior to the measurements, the catalysts were pretreated in air for 15 min at 673 K followed by a reduction by 4 vol.% H₂/N₂ at 673 K for 30 min. Subsequently, the reactor was quickly cooled down to room temperature under N₂ flow. After saturating the catalyst with 1% CO in N₂ for 1 h, weekly adsorbed CO was removed by purging the reactor with pure N₂ for 45 min. TPD in N₂ flow was performed with 20 K min⁻¹ up to a maximum temperature of 673 K. Gas concentrations of CO and CO₂ evolved during TPD were monitored by an IR detector (BINOS1000). For the estimation of the noble metal dispersion, an adsorption stoichiometry of 1:1 (CO:Pt) was assumed.

Assuming the supported noble metal particles are hemispherical in shape and Pd and Pt are distributed equally on the surface, particle diameters were calculated from dispersion. Based on structural parameters for the noble metals listed in [13] the following relation was used to calculate the mean particle diameter d_D (diameter derived by dispersion):

$$d_D = \frac{1.11}{D},$$

where D is the noble metal dispersion ($0 < D < 1$) and d_D is given in nanometers.

X-ray absorption measurements were performed ex situ and in operando by monitoring the catalyst bed under reaction conditions. At the Swiss–Norwegian Beamline (SNBL, BM01 beamline at ESRF, Grenoble) ex situ extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge spectra (XANES) of the fresh and deactivated samples loaded in a 2 mm quartz capillary were recorded at Pd K-edge (24.430 keV) in transmission mode. Additionally, the same samples were analyzed after reduction by 5% H₂/He at 373 K. Operando XAS experiments were performed for the catalyst-powder at the SAMBA beamline (SOLEIL, Paris) at the Pd K-edge (24.430 keV). The catalyst (sieve fraction 100–200 μm) was placed inside a 2 mm quartz capillary (20 μm wall thickness, 10 mm long catalyst bed). The structural properties of the catalysts were followed from room temperature (RT) to 1043 K using a hot air blower (FMB Oxford, cf. [7]) with 5 K min⁻¹ in a gas stream containing 4000 ppm CH₄, 10% O₂, 2% H₂O in He (flow of 50 mL min⁻¹). The outlet gas composition was monitored by a mass spectrometer. A similar experiment was repeated at the XAS-beamline at ANKA (Karlsruhe) at Pt L₃-edge (11.564 keV). For reasons of data quality larger capillaries of 3 mm in diameter were used. For maintaining the same space velocity the flow was adjusted to 80 mL min⁻¹. Additionally 6% of CO₂ were added to the gas mixture. Background removal, energy calibration, normalization and extraction of the EXAFS function as well as linear combination analysis was conducted using ATHENA and ARTEMIS of the IFFEFIT package [37].

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