

Desulfation of Pd-based Oxidation Catalysts for Lean-burn Natural Gas and Dual-fuel Applications

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ABSTRACT

Lean-burn natural gas (NG) engines are used world-wide for both stationary power generation and mobile applications ranging from passenger cars to Class 8 line-haul trucks. With the recent introduction of hydraulic fracturing gas extraction technology and increasing availability of natural gas, these engines are receiving more attention. However, the reduction of unburned hydrocarbon emissions from lean-burn NG and dual-fuel (diesel and natural gas) engines is particularly challenging due to the stability of the predominant short-chain alkane species released (e.g., methane, ethane, and propane). Supported Pd-based oxidation catalysts are generally considered the most active materials for the complete oxidation of low molecular weight alkanes at temperatures typical of lean-burn NG exhaust. However, these catalysts rapidly degrade under realistic exhaust conditions with high water vapor concentrations and traces of sulfur. The impact of sulfur poisoning and the regeneration of the degraded Pd-based oxidation catalyst by thermal and reductive regeneration were investigated. Thermal regenerations beginning at 500°C recover some catalyst performance when performed in the absence of sulfur. However, in an exhaust environment, where sulfur is always present at trace levels, thermal regeneration may prove impractical. Reductive regenerations successfully remove sulfur and recover catalyst activity, with sulfur removal occurring rapidly in the complete absence of O₂.

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INTRODUCTION

Lean-burn natural gas and dual-fuel (diesel and natural gas) engines are used world-wide for both stationary and mobile applications, and they continue to gain popularity due to the low cost of natural gas and the introduction of improved, purpose-built engines. However, the reduction of non-methane hydrocarbons (NMHCs) from the exhaust of these engines poses a challenge. While diesel engines emit very low concentrations of low molecular weight alkanes (e.g., ethane, propane, etc.), these species account for the majority of NMHCs emitted by lean-burn natural gas engines and a fraction equivalent to the natural gas substitution rate for dual-fuel engines. In addition, while currently unregulated for U.S. mobile sources, methane is a potent greenhouse gas and its emissions should be minimized where possible.

Palladium-based catalysts for the oxidation of low molecular weight alkanes have been an open research topic for the past 50 years [1]. While initial research in this area was motivated by energy production from the catalytic combustion of natural gas, more recent investigations have specifically targeted the catalytic oxidation of un-combusted alkanes in order to meet challenging regulatory requirements. The current U.S. Environmental Protection Agency (EPA) NMHC requirement for heavy-duty on-highway compression- and spark-ignition engines and nonroad compression ignition engines is 0.14 g NMHC/bhp·hr (0.19 g NMHC/kW·hr).

While there is general agreement that Pd-based catalysts are the most active for the complete oxidation of low molecular weight alkanes under lean exhaust conditions, research activities persist due to the significant shortcomings of these catalysts in real-world applications. The reactivity of supported palladium catalysts is inhibited by both water vapor and carbon dioxide present in exhaust gases and formed as a result of hydrocarbon oxidation over the catalyst [2, 3, 4]. Although, inhibition due to CO₂ can generally be neglected under exhaust conditions due to the larger inhibitory effect of water vapor [2]. It has been proposed that the reversible degradation from water vapor could be due both to the formation of inactive Pd(OH)₂ [2] and the interaction of hydroxide species with the metal support (e.g., Al₂O₃), interrupting oxygen transfer between the support and active Pd sites [3]. The impact of water vapor inhibition decreases substantially with increasing temperature, becoming small above 450°C due to the instability of surface hydroxides [2]. However, previous studies have focused on water concentrations lower than those in real-world exhaust (< 3 vol.%), and, thus, it is possible that hydroxide formation may have an impact at higher temperatures than those previously published. Reversible palladium deactivation also occurs due to the transformation of active Pd oxide (PdO) to inactive Pd(0) metal. Farrauto studied the decomposition of PdO/Al₂O₃ to Pd/Al₂O₃ and reported that the transformation occurs between 750 and 850°C in air and that re-oxidation does not occur until the temperature is reduced well below 650°C [5]. Catalytic degradation

studied the redox nature of a bimetallic Pt-Pd/Al₂O₃ catalyst and found that PdO reduction by CH₄ occurs between 225 and 300°C under the conditions studied [6].

Finally, sulfation of supported palladium catalysts has also been reported to have a detrimental effect on oxidation activity. Lampert et al. showed that as little as 1 ppm SO_x in exhaust gas can have a significant impact on oxidation of CH₄ [7]. Catalyst activity for NMHC oxidation was also affected but to a lesser extent. The authors found that sulfation occurs rapidly due to the selective adsorption of SO_x on Pd sites, but that the use of a sulfating support such as Al₂O₃ can slow the rate of Pd sulfation. More recently, Corro et al. showed that a pre-reduction step in 100% H₂ on a Pt-Pd/Al₂O₃ catalyst decreases the susceptibility of Pd to sulfation. Pt(0) metal sites, formed as a result of reduction, rapidly interact with SO₂, protecting active PdO sites [8]. Jones et al., investigating the recovery of various sulfated CH₄ oxidation catalysts, has shown that the activity of a model Pd/Al₂O₃ catalyst can be partially recovered by exposure to 100% H₂ at 400°C for 0.5 hr [9]. The authors speculate that this recovery is due to the reduction of surface sulfate species and the subsequent release of SO₂.

The sulfation and desulfation of a state-of-the-art Pd-based oxidation catalyst were evaluated in the present study to update previous work on model catalysts and with simplified gas mixtures. Activity is measured and presented as CO, CH₄, C₂H₆, and C₃H₈ lightoffs, while simulated exhaust gases intended to represent exhaust from a lean-burn natural gas engine also include NO, H₂O, and O₂. Both thermal and reductive catalyst regenerations are investigated, and the two methods are compared in terms of performance recovery, de-sulfation mechanism, and sulfur release.

EXPERIMENTAL

Catalytic activity, sulfation, and desulfation experiments were conducted with a catalyst core-reactor. The reactor has previously been described in detail [10], but a brief overview is provided below and a schematic of the system is shown in Figure 1. Briefly, the core-reactor used in this study consists of MKS™ mass flow controllers for gas metering, a Waters™ high performance liquid chromatography pump for water introduction, a Bronkhorst™ vapor delivery system for introduction of C₁₂H₂₆ (not included in the present study), a Lindberg™ 3-zone tube furnace for reactor temperature control, and a MKS 2030 HS Fourier transform infrared (FTIR) spectrometer for gas analysis. All lines are heated to approximately 190°C to eliminate condensation of water vapor and hydrocarbons. In addition, all FTIR calibrations were derived for gas-phase measurement at 191°C. The quartz reactor tubes used in this study were 39 inches (90 cm) long with inner and outer diameters of 1.1 inches (28 mm) and 1.26 inches (32 mm), respectively. The inlet 10 inches (25.4 cm) of the reactor were filled with 4 mm quartz beads to ensure that incoming gas is uniformly mixed and heated. All gases used in this study were provided by Airgas. Pure gases N₂ and O₂ were Ultra High Purity grade (99.999%), while two component hydrocarbon and NO mixtures in N₂ were National Institute of Standards and Technology (NIST) traceable Primary Standards.

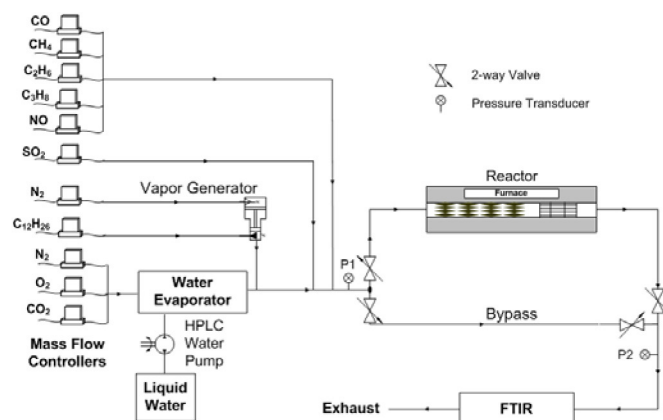


Figure 1. Schematic of catalyst core-reactor.

The oxidation catalyst evaluated in this study is a state-of-the-art Pd-based catalyst. The active materials (i.e., Pd and Pt) are dispersed on a high surface area alumina which is coated onto a cordierite substrate. Catalyst cores were 1" diameter by 1.5" long and were degreased at 650°C for 12 hours in 10 volume percent (vol.%) O₂, 11 vol.% H₂O, and balance N₂ prior to any evaluations. A 650°C degreasing temperature was selected because exhaust temperatures in lean-burn natural gas and dual-fuel engines can exceed 600°C.

Experiments can be separated into three different types: catalyst activity, sulfation, and desulfation. Catalyst activity was measured both with transient lightoff and steady-state isothermal experiments. Lightoff tests were conducted from 150 to 600°C at a temperature ramp rate of 5°C/min while steady-state activity was measured at 450, 500, 550, and 600°C. Gas concentrations for activity measurements were 10 vol.% O₂, 11 vol.% H₂O, 500 parts per million by volume (ppmv) NO, 1000 ppmv CO, 500 ppmv CH₄, 200 ppmv C₂H₆, 60 ppmv C₃H₈, and balance N₂, referred to as the standard gas mixture in this study. In addition, control experiments were conducted without H₂O to discern the impact of water vapor on catalyst activity and degradation.

Sulfations were conducted for up to 6 hours with the same concentrations as above and either 1 or 5 ppmv SO₂. Lampert et al. estimated the exhaust sulfur concentration of a lean-burn natural gas vehicle under both cruise and idle conditions, and the authors reported an average value of ~1 ppmv sulfur [7]. A concentration of 5 ppmv SO₂ is also used in this study to accelerate sulfation. Two desulfation strategies were investigated. Thermal desulfations were conducted in the same manner and with the standard gas mixture, with temperature holds at progressively higher levels. The efficiency of reductive desulfation was then investigated by periodically exposing the catalyst to only 11 vol.% H₂O, 500 ppmv NO, 500 ppmv CH₄, 200 ppmv C₂H₆, 60 ppmv C₃H₈, and balance N₂ at 450, 500, and 600°C. Reductive exposures had a duration of 10 minutes and the effect of O₂ concentration was also investigated. Since it is difficult to remove all traces of O₂ from real-world engine exhaust, concentrations of 0, 0.5, 1, 2, and 5 vol.% O₂ were evaluated. The catalyst was sulfated for 1 hr with 5 ppmv SO₂ in the standard gas mixture containing 10 vol.% O₂ in between each regenerative pulse