

IN SITU ACTIVATION FOR ENHANCED METHANE CONVERSION IN EMISSION CONTROL

Kyle A. Karinshak^{a,b*}, Patrick Lott^b, Michael P. Harold^a, Olaf Deutschmann^b

a University of Houston
Houston, TX 77054

b Karlsruhe Institute of Technology
Karlsruhe, Germany 76131

Abstract

The impact of H₂ pulses on Pd-Pt/La₂O₃-Y₂O₃-CeO₂-ZrO₂ and Pd-Pt/Al₂O₃ washcoated monolith catalysts under excessively lean conditions were investigated. Spatially-resolved mass spectroscopy and temperature probes were utilized to study temporal concentration and temperature gradients along the monolith length during transient operation. Modest catalytic activity improvements were observed under wet conditions when H₂ was pulsed over the catalyst in the constant presence of O₂, due to a sharp increase in temperature at the front of the catalyst. When H₂ and O₂ pulses were alternated over the catalyst, catalytic activity was shown to improve and remain stable over several hours under both dry and wet conditions above 315 °C. This improved catalytic performance persisted through subsequent experiments, resulting in lower light-off temperatures and extended catalyst activity with time on stream. The enhanced methane oxidation observed is the result of several separate effects occurring during the reductive pulse: removal of accumulated hydroxyl surface species, formation of metastable PdO-Pd complexes, and (in the case of Pd-Pt/CZ) the creation of oxygen vacancies in the support.

Keywords

Methane, Oxidation, Pulsing

Introduction

Lean-burn natural gas engines are a promising potential replacement for diesel engines due to the ubiquity of natural gas for fuel and the lower CO₂ and PM emissions resulting from natural gas combustion. Unfortunately, uncombusted methane – on the order of several hundred ppm – represents a significant emission control problem.

Previous research has shown that brief, periodic, reductive pulses during lean operation can not only regenerate sulfur-poisoned catalysts but can also stabilize catalytic performance above what it would otherwise be (A. Gremminger et al.; Arosio et al.). Bounechada et al similarly found that periodic rich pulses could recover catalytic activity lost due to water inhibition and that forced periodic operation resulted in higher and more stable

catalytic performance of a Pd-based catalyst (Bounechada et al.). Despite a number of studies into periodic operations of Pd-based, Three-Way Catalysts and some references to the beneficial effects of reductive pulses (Datye et al.; A. T. Gremminger et al.), there has been no substantial investigation into the potential effects and mechanism by which reductive pulses can benefit lean methane oxidation.

With this study we present a possible pathway of in situ activation of Pd-Pt/Al₂O₃ and Pd-Pt/La₂O₃-Y₂O₃-CeO₂-ZrO₂ (Pd-Pt/CZ) methane oxidation catalysts under different temperatures and gas compositions. Specifically, periodic reductive pulses of hydrogen are shown to result in two distinct effects dependent upon the system conditions.

Experimental and Results

Monolithic Pd-Pt/Al₂O₃ and Pd-Pt/CZ samples were tested by means of light-off experiments with and without H₂ under dry and wet lean conditions (10% O₂). Transient experiments consisting of periodic pulses of 1% H₂ were also performed. Two cases were examined: H₂ pulses with constant O₂, and H₂/O₂ switching. Spatially-resolved Mass Spectroscopy and FTIR were utilized to study changes in gas concentration over the length of the catalyst.

During H₂ pulsing with constant O₂, H₂ is converted to H₂O in an exothermic reaction, raising the temperature at the front of the catalyst by 60 °C. This increased temperature results in modestly increased methane conversion under wet conditions, likely a combination of a direct increase in conversion from the raised temperature as well as the desorption of water from active sites in the high-temperature area of the catalyst.

Alternating H₂/O₂ pulses resulted in recovered catalytic activity above certain temperatures; in some cases, activity was higher than without the reductive pulses. Furthermore, catalytic activity was enhanced during subsequent experiments. Figure 1 shows the reactivation of the Pd-Pt/CZ catalyst over time for methane oxidation. Figure 2 shows light-off curves for Pd/CZ after varying durations of H₂/O₂ pulses. The enhanced methane oxidation seen during H₂/O₂ switching results from the summation of several, simultaneous, independent effects occurring during the reductive pulse: removal of accumulated hydroxyl species, formation of metastable PdO-Pd complexes, and (in the case of Pd-Pt/CZ) the creation of oxygen vacancies in the support. EXAFS results from the Pd-Pt/CZ and Pd-Pt/Al₂O₃ samples show high concentrations of reduced Pd coexisting alongside PdO while TEM micrographs showed no more Pd-Pt alloying on the Al₂O₃ support but no significant change in metal dispersion for either catalyst.

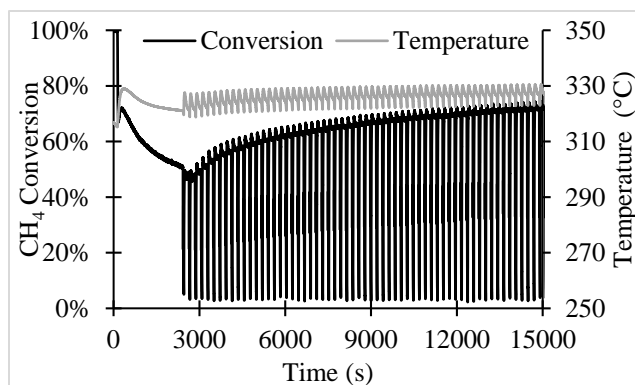


Figure 1. CH₄ conversion over time during H₂/O₂ pulses (30s/180s) at 315 °C.

Conclusion

The effects of reductive pulses are dependent upon the gas system and the catalyst support. With O₂ present, increased activity is due to thermal activation of the catalyst. When

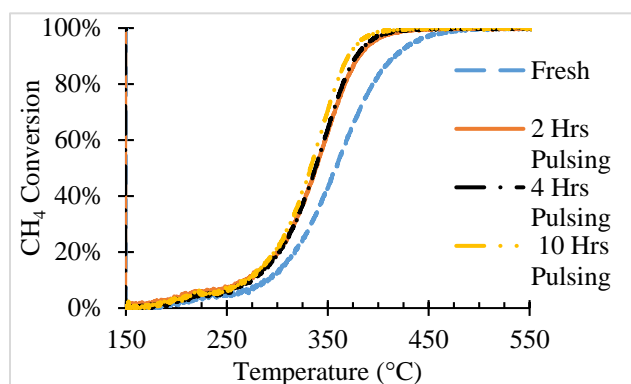


Figure 2. Pd-Pt/CZ light off curves after H₂/O₂ pulsing.

H₂ and O₂ alternate, several different effects occur at the same time: removal of accumulated hydroxyl species, formation of metastable PdO-Pd complexes, and (in the case of Pd-Pt/CZ) the creation of oxygen vacancies in the support. The effects activate the catalyst and prevent loss of activity over time.

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