Methane Oxidation Hystresis

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Introduction

With natural gas reserves growing, it is expected that the trend towards natural gas use for power applications and as a chemical precursor will continue to grow as well. Transporting the natural gas via pipeline requires intermittent compressor stations, where natural gas engines are used to repressurize the stream. These engines emit natural gas and NOx, as two of the primary pollutants. Natural gas powered vehicles have similar emissions issues. Two engine types for both of these applications are used, lean-burn and stoich/rich-burn. For these two, two catalyst technologies are used, one where there is an excess of oxygen is available, leading to primarily CH_4 combustion, and for the rich-burn engines, a three-way catalyst (TWC) approach is used. In terms of reducing CH_4 emissions, the operating conditions differ significantly, as do the kinetics and selectivities.

There has been significant research focused on CH_4 oxidation over Pd- and Pt-based catalysts, with Pd considered superior for the lean-burn applications [1]. Kinetic expressions have been derived, with 1st order in CH_4 and 0 order in O_2 commonly observed for lean conditions (oxygen excess), although lower orders in CH_4 have been observed with intermittent reducing (rich) conditions [2]. Water is known to have a significant inhibiting effect on performance, with reaction orders on the order of -1, with site competition the likely reason [3]. The reaction is typically modeled via a Langmuir-Hinshelwood approach. Hysteresis is often observed in exothermic reactions and was investigated in this study, with the intent of developing an engineering approach to attain high conversions at low temperatures.

Materials and Methods

Pt/Al_2O_3 was supplied by Umicore AG (95 g/ft^3 loading). All catalysts were Al_2O_3-supported and of monolith structure. The samples were 1" in diameter and 2.6" long. These were inserted into a tube reactor, with gases introduced using PraxAir mixtures and Bronkhorst flow controllers. Experiments were conducted to evaluate the effect of CH_4, O_2, NO and NO_2 concentration on performance. Reaction ignition and extinction were characterized using temperature programmed oxidation (TPO). A MKS MultiGas 2030 was used for gas concentration analysis

Results and Discussion

A monolith-supported Pt/Al_2O_3 catalyst was evaluated for CH_4 combustion under fuel lean and fuel rich mixtures using temperature programmed oxidation (TPO) and step-change temperature experiments. The experiments included performance evaluation during both ignition (increasing temperature) and extinction (decreasing temperature after ignition). Conversion hysteresis was observed, with the conversions during extinction higher than those during ignition under fuel lean or stoichiometric combustion reaction conditions (Figure 1). Results obtained demonstrate that this hysteresis effect can be used to achieve high CH_4 oxidation conversions at temperatures lower than that required for ignition, admittedly first through using high temperatures to obtain ignition, then lowering the temperature to take advantage of the hysteresis. Results also suggest that changing O_2 levels can lead to similar benefits. With the assumption that lean conditions and lower exhaust temperatures are associated with improved fuel economy, while higher exhaust temperatures and fuel rich conditions lead to higher CH_4 oxidation rates over the catalyst, the findings presented clearly demonstrate the potential to achieve both via a cyclic operating approach, with the frequency on the order of 10s of minutes. Data obtained when cycling between temperatures above and below the ignition point and between excess O_2 and stoichiometric O_2 levels proved this hypothesis.

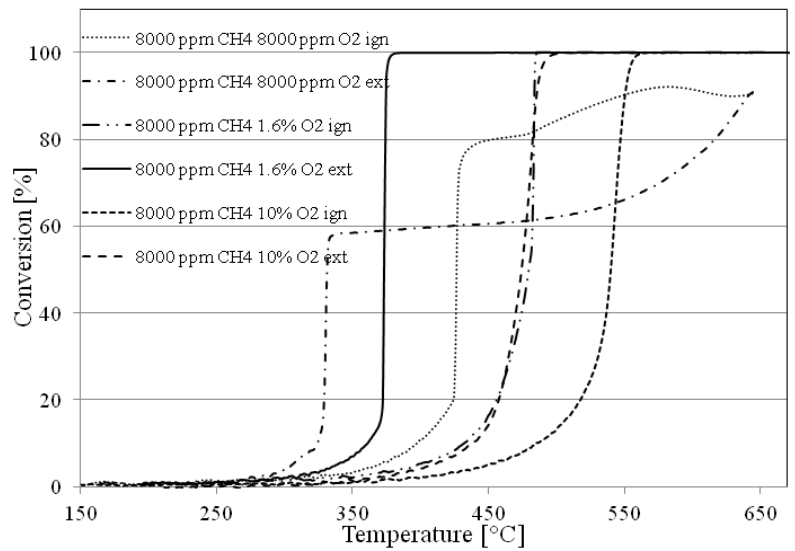

Figure 1. Catalyst performance during ignition and extinction stages of TPO experiments with different oxygen concentrations – heating/cooling rate of 7ºC/min and a reaction mixture of 8000 ppm CH_4 with 8000 ppm or 1.6% or 10% O_2.

Significance

With interest in natural gas for power applications growing (stationary and mobile), CH_4 emissions will be targeted. This study shows that the hysteresis effect can be used to maintain high CH_4 combustion conversions. After achieving light off, the temperature can be lowered resulting in improved fuel economies, or when conversions drop, the O_2 level can be lowered to reattain high conversions.

References

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