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Coupled methane and NO_x conversion on Pt + Pd/Al₂O₃ monolith: Conversion enhancement through feed modulation and $Mn_{0.5}Fe_{2.5}O_4$ spinel addition

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ABSTRACT

The performance of a dual-layer Pt-Pd/Al2O3 washcoated monolith promoted by an Al2O3-supported Mn_{0.5}Fe_{2.5}O₄ spinel base layer was evaluated with the objective to develop a catalyst with a lower loading of Platinum group metal (PGM) for stoichiometric natural gas vehicle (NGV) emission control. Flow reactor results show that a combination of a lean/rich modulated feed and spinel addition gives enhanced methane and NO conversions compared to a steady-state feed having the same overall composition. Washcoated catalysts - PGMonly, spinel-only, PGM + spinel - were compared over a wide range of operating conditions. The results show a decrease in the methane conversion light-off temperature of up to 85 °C for an application-relevant feed (CH₄ + NO + H_2 + CO + O_2 + H_2O + CO_2) while a moderate 40 °C decrease was observed for a simple feed (CH₄ + O_2 + H₂O + CO₂). In the absence of spinel the modulation enhancement is negatively impacted at high methane conversion (> 80 %). The data show that the O_2 storage and release property of the spinel is needed to fully exploit the modulation enhancement. The mechanism responsible for the enhancement is linked to suppression of O₂ inhibition on the methane oxidation rate near the stoichiometric neutral point ($\lambda = 1$). Sufficiently fast cycling achieves a balance between a metallic and oxidic precious metal crystallites favorable for methane activation. The addition of spinel moves this balance closer to the $\lambda = 1$ feed, enabling a high oxidation efficiency with lower byproduct NH₃ selectivity. Enhancement in the NO conversion follows the methane conversion due to an easier NO reduction under the slightly rich of stoichiometric feed. Comparison of the PGM + spinel catalysts to PGM-only catalysts shows that the addition of spinel in combination with modulation can achieve the same activity with a lower PGM loading.

1. Introduction

Abundant recoverable natural gas reserves motivate interest in the use of natural gas (NG) as a transportation fuel. However, stoichiometric combustion of natural gas produces excessive slip of greenhouse gas (GHG) CH₄ along with emission of nitrogen oxides (NO_x: NO, NO₂). Emerging GHG regulations require control of CH₄ emissions for NG-fueled vehicles [1]. However, complete oxidation of CH₄ over the conventional Platinum group metal (PGM)-based three-way catalyst (TWC) is ineffective, with typical light off temperatures over commercial TWC formulations exceeding 500 °C under application-relevant conditions [2]. Simultaneous conversion of CH₄ and NO requires an exhaust that is a near-stoichiometric mixture of air and fuel ratio ($\lambda \approx -1$; where λ is the lean/rich ratio). As a result, CH₄ slip increases O₂

levels, exacerbating NO_x emissions due to ineffective NO_x reduction in unreacted O₂. It has been reported that modulation between lean ($\lambda > 1$) and rich ($\lambda < 1$) feed gas enhances catalytic performance, and that the conversion of CH₄ and NO is more pronounced when the feed is slightly rich of stoichiometric [3,4].

Conventional formulations of the CH₄ oxidation catalyst (MOC) are PGM-based. Various combinations of Pt, Pd, and Rh are coupled with an oxygen storage/release material, such as ZrO_2 -stabilized CeO₂ (CZO) which acts as an oxygen buffer through the redox cycle of Ce⁴⁺/Ce³⁺ [5,6]. In addition to these ceria-containing catalysts, there has been growing interest in multicomponent transition metal oxides with an ordered crystallographic spinel structure of the formula AB₂O₄. Selected spinels have superior oxygen storage capacity (OSC) and may synergize with the PGM function. A wide range of oxygen states can be

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generated at both the tetrahedral "A" site and the octahedral "B" site of the spinel. Xie et al. reported that oxygen vacancies in selected spinels can be readily generated even at room temperature [7].

Emission control catalysts operate under inherent transient conditions brought about by the vehicle operation. Moreover, the control of the fuel-air mixture relies on feedback control from the lambda (λ) sensor [8]. A result of the λ control system is the occurrence of rapid (~1 Hz) modulation or "dithering" in the fuel-air ratio around the desired set point. Silveston [8] reviewed the earlier works which showed that under some conditions the performance under a modulated feed can exceed that under steady state conditions. Muraki et al. [9] reported enhancement in NO reduction on a Pd catalyst containing an O_2 storage component during periodic operation. Hoebink et al. [10] conducted experiments of CO oxidation in a fixed bed of Pt/Al₂O₃ catalyst pellets. The experiments and elementary step kinetic scheme model showed that there exists a window of forced periodic frequencies in which the CO conversion is enhanced. The role of intraparticle diffusion was also assessed. Koci et al. [11] analyzed, through a model, the contribution of diffusion in the washcoat in a three-way catalytic converter during O₂ feed concentration modulations.

With the high cost of Pd and Pt, there is a need to develop more active MOCs with lower PGM loading and which are therefore more cost-effective. In this study, we examine the catalytic performance of a spinel-promoted Pt/Pd catalyst for the stoichiometric oxidation of CH₄. The performance of a PGM + $Mn_{0.5}Fe_{2.5}O_4$ spinel dual-layer wash-coated monolith is evaluated under steady-state and lean/rich modulation feed conditions. The results show significant CH₄ conversion enhancement with modulation using the multi-component catalysts at conversion levels not obtainable with the individual catalyst component. Experiments are described that elucidate the catalytic performance enhancement for converting CH₄ and NO_x. Finally, a mechanistic picture is proposed that is consistent with the catalyst performance features and conversion enhancement.

2. Materials and methods

Three types of washcoated monolith samples were provided from CDTi (Oxnard, CA), and are depicted in Fig. 1. These included duallayer PGM (top layer) + spinel (bottom layer) samples, dual-layer PGM-only samples, and a single-layer spinel-only sample. The top layer consisted of PGM (20 or 30 g/ft³ monolith) with a 19:1 ratio of Pt:Pd supported on high surface area alumina, while the base layer comprised an Al₂O₃-supported Mn_{0.5}Fe_{2.5}O₄ spinel (25 wt.%). Both layers had total loadings of 100 g/L. As listed in Table 1, two PGM-only catalysts

PGM+Spinel (30/100)



Fig. 1. Configuration of washcoated monolith samples.

were used and are denoted by (30/0, 40/0) while a single spinel-only (0/100) catalyst was used. All of the samples had a 600 cpsi (cells per square inch) Cordierite substrate. Monolith core samples had a 1" diameter and 0.85" length.

Each of the tested monoliths was contained in a quartz tube which was placed in a tube furnace. Two thermocouples were placed in the tube to measure the temperatures of the inlet gas and the back of the monolith sample. The gas hourly space velocity (GHSV) was 40,000 h⁻¹ (@ STP), with a total flow rate of 7.2 standard L/min. The conversions of CH₄, CO, NO_x and yields of N-containing products including NO₂, N₂O and NH₃ were measured for each of the samples using a FTIR (MKS model MultiGas 2030). Two feed conditions were used; (i) steady-state ($\lambda = 0.992$, 0.993) and (ii) modulated lean (1.5 s)-rich (1.5 s) ($\lambda = 0.978$ –1.006, 0.980- 1.006, both at 0.33 Hz), depicted in Fig. 2. The lean/rich ratio parameter Lambda (λ) is defined as follows:

$$\lambda = \frac{0.5 \left[(\text{CO}) + 2(\text{O}_2) + (\text{NO}) + (\text{H}_2\text{O}) + 2(\text{CO}_2) \right]}{\left[(\text{CO}) + (\text{CH}_4) + (\text{CO}_2) \right] + 0.25 \left[2(\text{H}_2) + 4(\text{CH}_4) + 2(\text{H}_2\text{O}) \right]}$$
(1)

This definition considers all sources of O to be oxidizing and all sources of C and H to be reducing. For the modulated feed experiments two setups were used. The testing of the light-off curves employed a four-way switching valve (Valco Instruments Co. Inc) setup. The procedure was designed to achieve a constant total flow rate of 7.2 standard L/min, such that the change of O_2 concentration was simultaneously compensated by switching N_2 flow.

The catalytic performance was tested with both a "simple feed" (1500 ppm CH_4 + 1950 ppm O_2) and a "full feed" (1500 ppm CH_4 , 8000 ppm CO, 1000 ppm H_2 , 1000 ppm NO added) with O_2 at 5650 ppm (steady-state feed) or 3400 ppm (1.5 s) and 7900 ppm (1.5 s) (modulated feed). Each feed contained 10 % CO_2 + 10 % H_2O and balance N_2 . Feed concentrations are listed in Table 2. The full feed emulates an exhaust from a stoichiometric NGV. The simple feed conditions were close to the average λ and modulation amplitude of the full feed. Prior to each test, the monolith sample was pretreated with the feed mixture identical to that of the steady state feed at 500 °C for 30 min. The reported data under both steady state and modulation conditions were obtained after waiting for 20-30 min to ensure a constant condition. The reported modulation results are time-independent, time-averaged values over the course of many cycles.

Lambda sweep experiments were performed on a PGM-only and PGM + spinel catalyst. The experiments were carried out at three temperatures, defined as the inlet temperature under inert flow: 345 °C, 415 °C, and 490 °C. The average lambda was swept from 0.980 to 1.012, in increments of 0.004, with an additional data point collected at 0.972. Lambda sweeps were carried out at under modulated and steady-state conditions.

3. Results and discussion

3.1. Effect of feed modulation on catalytic performance

In the first set of experiments, the modulation impact was assessed by comparing the steady-state operation to lean/rich switching for the 30/100 catalyst [PGM (30 g/ft^3) + spinel (100 g/L)].

The simple feed results show that the cycle-average CH₄ conversion with modulation (blue circles) exceeds the steady state conversion (red triangles) in the vicinity of the light-off (Fig. 3(a)). Specifically, the light-off temperature (T₅₀, temperature giving 50 % CH₄ conversion) decreases by ~40 °C; i.e., T₅₀ (steady state) ~ 525 °C compared to T₅₀ (modulated) ~ 485 °C. The beneficial effect of the modulation on the CH₄ conversion is clearly seen in Figs. 3(c) and (d), which compare the time-dependent CH₄ conversion without and with modulation at a fixed inlet temperature of 500 °C. The CH₄ conversion is 33 % under steady-state operation compared to a cycle-average value of 55 % under modulation. Note that the periodic variation in the CH₄ conversion

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Table 1

Information on the monolith catalysts used in study.

Monolith Sample		PGM Loading (g/ft ³)	Spinel Loading (g/L)
Dual-layer PGM + Spinel (20/100, 30/100, 30/60)	Top layer (PGM only) Layer loading: 100	20, 30 ^a	0
	Bottom layer (Spinel only) Layer loading: 100 g/L	0	100 ^b
Dual-layer PGM-only (30/0, 40/0)	Bottom layer (Alumina) Layer loading: 100 g/L	30, 40 °	0
Spinel-only (0/100) Layer loading: 100 g/l (Single Layer)		0	100

^a Pt:Pd-19:1/Al₂O₃.

^b Mn_{0.5}Fe_{2.5}O₄ Spinel (25 wt.%)/Al₂O₃ (75 wt.%).

 c 30/0 sample has a bottom layer loading of 60 g/L, the 40/0 sample has a bottom layer loading of 100 g/L.



Fig. 2. Steady-state ($\lambda=0.992)$ and modulated rich ($\lambda=0.978,\ 1.5\,s)/lean$ ($\lambda=1.006,\ 1.5\,s)$ feeds.

between \sim 50 % and 60 %, reflects the feed modulation of 1.5 s lean/ 1.5 s rich cycling; i.e., a period of 3 s.

With the simple feed containing only CH_4 and O_2 plus background gases the main desired reaction is the complete oxidation of CH_4 :

R1: $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

Partial oxidation product CO was detected during the modulated feed experiment as seen by the data in Fig. 3(b). Its formation is via the partial oxidation and/or steam reforming of CH_4 :

R2: $CH_4 + H_2O \longleftrightarrow 3 H_2 + CO$

R3: $CH_4 + 0.5 O_2 \leftrightarrow 2 H_2 + CO$

Formation of CO implies the generation of H_2 which is not detectable by the FTIR. The water gas shift reaction also occurs which modifies the CO/CO₂ ratio:

R4: CO + H₂O
$$\leftarrow \rightarrow$$
 H₂ + CO₂

As stated earlier, the full feed mixture simulates NGV exhaust gas by additionally containing CO, H_2 and NO (Table 2). Fig. 4 shows the performance data obtained without (blue circles) and with modulation

(red triangles). Figs. 4(a) - (c) show the measured CH₄, CO, and NO conversions while Figs. 4(d) - (f) show the effluent concentrations of N-containing products NO₂, NH₃, and N₂O.

Consider first the steady state results. The three feed components CO, NO, and CH₄ were oxidized in the order CO ($T_{50} \sim 260$ °C), NO ($T_{40} \sim 300$ °C), CH₄ ($T_{50} \sim 480$ °C). (The H₂ in the feed is assumed to have fully oxidized over Pt at ambient temperature. This is distinguished from H₂ that was generated at higher temperature by methane steam reforming or water gas shift.) The oxidations of CO and NO are given by

R5: CO + 0.5
$$O_2 \rightarrow CO_2$$

R6: NO + 0.5 $O_2 \leftrightarrow O_2$

Note that the NO conversion exhibits a local maximum due to its reversibility in this range of temperature. This is further evidenced by the NO₂ concentration data which has a similar nonmonotonic dependence on temperature (Fig. 4(d)). The maximum NO conversion (~40 %) occurs at an inlet temperature of ~300 °C. For temperatures exceeding 500 °C the NO is completely consumed. This is a result of the high CH₄ conversion consuming the O₂ which leads to a reducing condition that is favorable for NO reduction according to the reactions

The steady state effluent NH_3 concentration is close to zero for most temperatures with the exception of high temperature (> 475 °C) and a narrow temperature range between 200 and 260 °C. Finally, N₂O (Fig. 4(f)) shows a similar nonmonotonic dependence as NO_2 but with a maximum concentration that is about 50 % lower. In contrast to NO_2 which is related to the aforementioned reversibility, the N₂O maximum is attributed to the balance between N–O bond scission, NO desorption, and NO reduction with contributing reactions given by

R10:	NO	+	0.5	$H_2 \rightarrow$	· 0.5	N_2O	+	0.5 H ₂	0
R11:	NO	+	0.5	co –	× 0.5	N_2O	+	0.5 C	O_2

Table 2

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reeas	COMPOSITIONS	with	and	without	modulated	reed	condition.	

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Steady-state Feed ^a (20 min. at fixed inlet temperature)	Simple Feed w/o modulation	Simple Feed w/ modulation	Full Feed w/o modulation	Full Feed w/ modulation
	$\lambda = 0.993$	$<\lambda>=0.993~(0.980-1.006~at$ 0.33 Hz)	$\lambda=0.992$	$<\lambda>=0.992$ (0.978–1.006 at 0.33 Hz)
CH ₄	1500 ppm	1500 ppm	1500 ppm	1500 ppm
CO	0 ppm	0 ppm	8000 ppm	8000 ppm
H ₂	0 ppm	0 ppm	1000 ppm	1000 ppm
NO	0 ppm	0 ppm	1000 ppm	1000 ppm
O ₂	1950 ppm	0 ppm (1.5 sec) / 3900 ppm (1.5 sec)	5650 ppm	7900 ppm (1.5 sec) / 3400 ppm
				(1.0 300)

 $^a\,$ Background gas: 10 % H_2O, 10 % CO_2 and N_2 balance.

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Fig. 3. Catalytic performance of 30/100 catalyst for a simple feed. (a) and (b) show the dependence of the cycle-average methane and CO on the inlet temperature, while (c) and (d) show instantaneous methane conversion and catalyst temperature for an inlet temperature of 500 °C without and with feed modulation, respectively.

Enhancement in the CH₄ conversion was observed for the full feed (Fig. 4(a)) as it was for the simple feed (Fig. 3(a)). For both steady-state and modulated operation the expected sigmoidal dependence of conversion on inlet temperature is evident. The conversion enhancement is more pronounced for the full feed as compared to the simple feed. For the full feed, a decrease in the light-off temperature of ~85 °C was obtained; i.e., the T₅₀ with modulation of 395 °C compares to 480 °C without modulation. This compares favorably to the modest light-off temperature decrease of ~40 °C for the simple feed. The larger enhancement of CH₄ conversion by modulation for the full feed is attributed to differences in the effective CH₄/O₂ feed ratio. We define the stoichiometric number, S_N as

$$S_{N} = [2(O_{2}) + (NO)] / [4(CH_{4}) + (CO) + (H_{2})]$$
(2)

such that $S_N<1$ is rich and >1 is lean. For the simple feed, the cycle averaged $S_N=0.65$ whereas for the full feed the cycle averaged $S_N=$

0.82. At the temperature needed for the light-off of CH₄, assuming both CO and H₂ are completely consumed, $S_N \sim [2(5650 - 4000 - 500) + 1000)/[4(1500)] = 0.55$. Thus, the full feed has a richer cycle-average oxidant to reductant ratio. (Note this comparison is only valid in the intermediate temperature regime in which CO and H₂ are completely consumed and steam reforming is negligible, allowing H₂O to be ignored as an oxidant in the S_N definition.) This impacts the extent of enhancement by the modulation. The best ratio is the one giving a maximum methane oxidation rate (conversion) at the given temperature and modulation amplitude. As we show later, variation of λ (or S_N) can locate that ratio. The impact of amplitude and frequency will be reported in a future study.

The beneficial impact of the modulation was not encountered for CO oxidation (reaction R5). As shown in Fig. 4(b), essentially the same CO oxidation light-off temperature is evident with and without feed modulation. This is attributed to the presence of sufficient oxygen available



Fig. 4. Catalytic performance of 30/100 catalyst under full feed condition as a function of temperature.

to react with CO in the temperature under 300 °C, well below that of CH₄ oxidation light-off. That is, the outlet O₂ concentration without modulation is nearly identical to the cycle-average O₂ concentration under the periodic lean/rich condition.

For NO conversion, a qualitatively different trend was obtained for both the steady-state and modulated feeds (Fig. 4(c)). Without feed modulation, the NO light off starts at ~250 °C, then exhibits a maximum conversion at 300 °C, which is attributed to the reversible NO oxidation (reaction R6). The decrease in the NO conversion is due in part to the increase in rate of the reverse reaction at higher temperature leading to a maximum in the NO₂ formation. However, given that the NO2 concentrations with and without modulation are comparable, the NO2 decomposition explanation does not completely account for the data. A contributing factor may be a lower PGM activity suppressed by the plentiful O₂ available due to the low CH₄ conversion. Under modulating conditions a higher CH₄ conversion lowers the O₂ concentration thereby avoiding the PGM activity suppression effect. The second NO light off encountered in the higher temperature regime, \sim 445 °C, is a result of the reaction between NO and the H₂ and CO produced from CH4 steam reforming, reaction R2 [12]; i.e. reactions 8a and 8b The rich conditions lead to the production of NH₃ as shown in Fig. 4(e) or N₂ (not measured). The feed modulation significantly decreases the $T_{50,NO}$ value (~ 365 °C), compared to the $T_{50,NO}$ of 480 °C obtained for the steady-state feed. The concurrent enhancement of the NO and CH₄ conversions is attributed to the reduction of NO by partially oxidized species H₂, CO, and CH_x surface fragments.

It is instructive to locate the onset of O_2 depletion since this point demarcates catalytic oxidation chemistry from catalytic reduction chemistry. Since O_2 is not measurable with the FTIR the depletion point can only be estimated. Fig. 5 shows the dependence of the estimated "remaining O_2 concentration" as a function of inlet temperature. Using the CH₄ and CO conversion measurements, and utilizing the stoichiometry of the following global oxidation reactions R1, R5, and R6, along with H₂ oxidation:

R12:
$$H_2 + 0.5 O_2 \rightarrow H_2O$$

an estimate of the effluent O_2 concentration can be obtained using the expression

$$C_{02}(z = L) = C_{02}, \text{ in } -\sum_{i=1}^{4} \nu_i C_{i,in} X_i$$
 (3)

where C_{O2} is the unreacted O_2 concentration, $C_{O2,in}$ is the inlet O_2 concentration (cycle average value for modulated feed), $C_{i,in}$ is the inlet



Fig. 5. Estimated O₂ concentration at the effluent of the monolith.

concentration of feed component i (i = CH₄, CO, NO, H₂), ν_i is the O₂ stoichiometric coefficient in reaction R1 (I = 1), R5 (I = 2), R6 (I = 3), and R12 (I = 4), and X_i is the measured fractional conversion of component i. Note that for NO oxidation we can use the measured NO₂ concentration; i.e. C_{NO,in} X_{NO} = C_{NO2}. In applying eqn. (3) it is assumed that H₂ fed is completely consumed.

The estimated $C_{O2}(z = L)$ values are shown as a function of the inlet temperature using the full feed, under both the steady state and modulation. The modulated feed has the same O_2 concentration fed over a full cycle as the constant value for the steady state feed (5650 ppm).

The steady state feed results show that O_2 is depleted at an inlet temperature of ~460 °C. At this point the CH₄ conversion reaches ~85 % and CO conversion is 100 % as shown in Figs. 4(a) and 4(b), respectively. Moreover, the formation of NH₃, along with the complete conversion of NO at 500 °C and higher, suggests reaction between NO and H₂ (R7, R8) and CO (R9). While N₂ is not measureable with the FTIR, its presence can be determined by an overall N balance. The H₂ is generated from a combination of steam reforming, partial oxidation of CH₄ (reactions R2 and R3), and water gas shift (R4).

With feed modulation the O₂ is estimated to be depleted at the lower temperature of ~360 °C. Here, the CH₄ conversion is ~50 % (Fig. 4(a)). As the temperature increases further the CH₄ conversion increases sharply and approaches the nearly constant value of ~90 % at ~520 °C and higher. Under modulation NH₃ formation is much higher due to the increased generation of H₂ and its reaction with NO (Fig. 4(e)). The higher NH₃ concentration levels off at higher temperature which underscores, but does not fully explain, the complete consumption of NO (Fig. 4(c)). NO may be reacting as an oxidant once O₂ is depleted during modulation – given the large amount of N₂ produced. While not measured, breakthrough of unreacted H₂ is anticipated under these anaerobic conditions in the downstream section of the monolith [14]. Additional experiments are underway to confirm these conjectures as part of the development of a predictive monolith reactor model.

Fig. 6 shows the instantaneous conversions of CH₄ and NO as a function of time, comparing the steady-state and modulated feed conditions at an inlet temperature of 385 °C. The CH₄ conversion is negligible, and only 25 % of the NO conversion is attained with the steady-state feed. In contrast, during modulation enhanced CH₄ and NO conversions vary periodically in the range of ~35 to 55 % and 72–78%, respectively. Note that the conversions of CH₄ and NO are nearly perfectly synchronized with the lean/rich cycling. This indicates that the consumption of CH₄ leads without delay to the consumption of NO under these conditions. H₂ generated by CH₄ partial oxidation (R2) and methane steam reforming (R3) react with NO. Finally, the outlet concentration of byproduct NH₃ exhibits up-and-down behavior as a

Fig. 6. Comparison of CH_4 and NO conversions of 30/100 catalyst as a function of time for (a) steady-state and (b) modulated feed.

function of the modulation similar to that of NO and CH_4 conversion shown in Fig. 6b.

3.2. Effect of spinel on catalytic performance

To investigate the effect of spinel on the catalytic performance, three monolith samples PGM + spinel (30/100), PGM-only (30/0) and spinel-only (0/100), were evaluated under steady-state and modulated feed conditions. The comparison results are shown in Fig. 7. [As noted in the Experimental section, the washcoat loadings of the PGM and spinel functions in the dual layer (Top layer: 30 g PGM/ft³ @ 100 g PGM layer/L; Bottom layer: 100 g spinel/L) are identical to the loadings of each in the single-layer catalysts [PGM-only: 30 g PGM/ft³ @ 100 g PGM layer/L; spinel-only: 100 g spinel/L).]

Under steady-state conditions, the light-off of CH₄ and NO occurred at T(X = 20 %) ~450 °C for both the 30/100 and the 30/0 catalysts. However, a higher overall conversion of CH₄ was achieved by the 30/0 sample compared to the 30/100 sample. A negative interaction between the spinel and PGM at the washcoat interface under the continuous, slightly rich feed condition could be a contributing factor. (In results not shown here, PGM supported directly on spinel leads to worst catalytic performance.) In this regime of complete O_2 conversion, the spinel may affect the CO vs. CO₂ product selectivity, thereby impacting the CH₄ conversion. Contribution by increased washcoat diffusional resistance in the dual-layer 30/100 sample cannot be ruled out although this would seem unlikely given that the PGM is located in the top layer closest to the flowing gas. The 30/0 catalyst exhibited heightened CH₄ conversion under a modulating feed at lower inlet temperatures (> 450 °C) compared to steady state operation. However, the difference in the CH₄ conversion with and without modulation decreased at higher inlet temperatures (> 450 $^{\circ}$ C). In contrast, the 30/ 100 catalyst exhibited a larger decrease in the CH₄ light-off temperature with the switch from a steady-state to modulating feed, and that difference was sustained at higher temperatures. Finally, the CH₄ oxidation activity for the spinel-only catalyst (0/100) was negligible over the temperature range employed in this study. These findings clearly show ARTICLE IN PRESS

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Fig. 7. Effect of lean/rich modulation for full feed on catalytic performance over dual-layer PGM + Spinel (30/100), single-layer PGM-only (30/0) and single-layer Spinel-only (0/100) monoliths.

a beneficial impact of the MFO spinel on the enhancement of CH_4 oxidation during feed modulation.

The conversion of NO is closely coupled with the CH_4 conversion through the availability of O_2 . The enhancement of CH_4 conversion has the effect of reducing the gas phase O_2 concentration. This in turn enables enhanced NO decomposition and reduction under richer conditions. As seen in Fig. 7, the Pt-Pd catalysts with and without MFO spinel show no big difference in the NO conversion below 300 °C, regardless of the feed conditions, when the CH_4 oxidation is negligible. This reflects that the NO conversion by oxidation at lower temperature region is insensitive to the lean/rich perturbation. It is noted that the NO conversion obtained with the spinel-only catalyst is also negligible over the entire range of the temperature employed. Under the modulation condition, the 30/100 catalyst with spinel achieved full conversion of the NO at 440 °C and above, while an incomplete conversion in range from 65 ~ 85 % was observed over the PGM-only 30/0 catalyst.

Fig. 8 compares the performance of dual layer PGM + spinel catalysts to PGM-only catalysts. Two PGM loadings were considered in combination with the MFO spinel, 30/100 and 20/100. These were compared against two catalysts with higher PGM loadings and no spinel (40/0 and 30/0). Fig. 8(a) compares the CH₄ conversion obtained with the 20/100 and 30/0 catalysts for the full, modulated feed. Within experimental error, the two catalysts have nearly the same CH₄ oxidation light-off performance at conversions below 50 %. In a narrow range of temperature (400–480 °C) the 20/100 catalyst slightly outperforms the 30/0 catalyst. At temperatures exceeding 480 °C the 30/0 is slightly more active. Thus, the addition of the MFO spinel to a lower loading of PGM (20 g/ft³) is equivalent to ~10 g PGM/ft³ in terms of methane oxidation activity. Thus, addition of the spinel to the PGM catalyst can reduce the amount of PGM needed in catalysts compositions.

While the comparison between the 20/100 and 30/0 is favorable towards the spinel-added catalyst, higher loadings of PGM may outweigh the benefits that the spinel provides. Although the 30/100 PGM-

Fig. 8. Effect of lean/rich modulation for full feed on catalytic performance over (a) PGM + Spinel (20/100) and PGM-only (30/0) and (b) PGM + Spinel (30/100) and PGM-only (40/0) monoliths.

spinel sample under modulation outperforms the 40/0 PGM-only sample under steady-state conditions, it is outperformed for all temperatures when the PGM-only sample is subject to the modulated feed, as seen in Fig. 8b. For all samples, the methane conversion is incomplete at high temperature. Given that the full feed is slightly net rich ($\lambda = 0.992$), this is to be expected. The limiting methane conversion depends on the product selectivity. In the high T regime, O2 is depleted and anaerobic chemistry occurs, including methane steam reforming (R2). This explains why the CO conversion exhibits a maximum; i.e. reforming generates CO and H₂, while the water gas shift reaction (R4) impacts the relative concentrations of CO and CO₂. It is noted in Fig. 8b that the PGM-only 40/0 catalyst has a higher limiting CH₄ conversion than the spinel-containing 30/100 sample. This can be explained by a difference in the PGM loading of the two samples. While the addition of spinel can shift CH₄ oxidation into more-favorable, lower temperature regimes for light-off, Figs. 7 and 8 show the presence of spinel does not lead to a higher limiting CH₄ conversion.

3.3. Mechanism Considerations: Modulation + Spinel

The enhancement afforded by the lean/rich switching is a result of the coupling between the nonlinear dependence of the CH₄ oxidation rate on O₂ and the periodically varying gas phase composition. Experiments were carried out over a range of O₂ feed concentrations for both the PGM-only and PGM + spinel catalysts. Fig. 9 shows the dependence of CH₄ conversion on the feed lambda (λ) data for the PGM-only catalyst under both steady state and modulated feeds. At 490 °C, the conversion exhibits a maximum at an intermediate λ value with a sharp fall-off occurring near the stoichiometric neutral point ($\lambda = 0.992$). That is, the methane conversion increases with O₂ concentration up to a point but then decreases sharply due to inhibition of active sites by adsorbed oxygen. For lower temperatures, this trend holds true but is shifted leftward.

When the PGM-only catalyst was exposed to a modulated feed

Fig. 9. Dependence of methane conversion on λ . Comparison of steady-state and modulated feed for PGM-only monolith (30/0).

 $(A = 2\Delta\lambda = 0.028)$ over a range of cycle-average lambda values $(<\lambda >)$, the performance of the catalyst improved for most of the $<\lambda >$ values. The exception is points at very rich conditions and low temperatures under steady-state conditions, where performance suffered. As before, these results demonstrate that even without spinel a benefit is achieved for methane conversion by feed modulation.

Similar experiments conducted on the PGM + spinel catalyst were conducted to investigate the impact of the spinel. Fig. 10 compares the PGM-only to the PGM + spinel; as mentioned earlier, both catalysts have the same 30 g/ft³ PGM loading while the PGM + spinel has a base layer containing 25 % of the $Mn_{0.5}Fe_{2.5}O_4$ spinel (remainder Al_2O_3). The base layer of the PGM-only sample contains only Al_2O_3 .

The comparison shows a clear benefit of the spinel addition. An increase in the maximum CH₄ conversion is obtained for the lowest temperature, 345 °C. An important effect of the spinel is to move the CH₄ conversion maximum to a higher $< \lambda >$ range. In doing so, the maximum CH₄ conversion was obtained at $< \lambda > = 0.996$ for the PGM + spinel sample. This finding is noteworthy because the by-product NH₃ is lower at this point compared to the NH₃ produced by PGM-only sample, as seen in Fig. 11.

These experimental findings suggest that the CH_4 oxidation is a complex function of the time-varying CH_4 and O_2 concentration with non-negligible conversion enhancement possible, particularly if spinel is present. Here we conjecture on the likely underlying mechanism.

A key contributing feature of CH₄ oxidation is the nonlinear

Fig. 10. Dependence of methane conversion on feed lambda. Comparison of modulated feed for PGM-only (30/0) and dual-layer PGM + Spinel (30/100) monoliths.

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Fig. 11. Dependence of NH₃ formation on feed lambda. Comparison of modulated feed for PGM-only (30/0) and dual-layer PGM + Spinel (30/100) monoliths at 490 °C. The square points at the $< \lambda >$ of maximum CH₄ conversion for the two catalysts.

dependence of the CH₄ oxidation conversion on the O₂ concentration. The maximum in the CH₄ conversion at an intermediate O₂ concentration (lambda) has been previously reported. Oh et al. [13] reported a nonmonotonic dependence of CH₄ conversion on O₂ near the stoichiometric point for Pt, Pd and Rh catalysts. Bugosh et al. [14] reported a similar nonmonotonic dependence and even the existence of multiple states in the form of a clockwise hysteresis. They attributed the data to the inhibition of CH₄ oxidation by oxygen due to the stronger adsorption of oxygen than methane on both metallic Pt and Pd. Burch and Loader [15] showed an increasing dependence of the steady-state CH₄ oxidation light-off temperature with increasing O₂/CH₄. This infers a negative-order dependence on O₂.

The mechanistic origin of the nonmonotonic dependence of CH_4 conversion on the O_2 concentration is attributed to mixed-phase metallic Pt + Pt oxide, denoted by Pt-PtO. Chin et al. [16] showed that a key step in Pt-catalyzed CH_4 oxidation is the abstraction of the first hydrogen from CH_4 . This CH_4 activation step is enhanced at the Pt-PtO site due to the favorable formation of Pt - OH. The energy barrier for CH_3 formation is therefore lower, which increases the oxidation rate. Once formed, CH_3 reacts rapidly, forming a mixture of CO, H_2 , CO_2 , and H_2O . Thus, an intermediate coverage of Pt-O maximizes the CH_4 activation. On the other hand, too high a Pt-O coverage leads to a reduction in the activation rate.

The beneficial impact of modulation on the CH₄ conversion is result of a nonlinear coupling between the oxidation rate inhibition by O₂ and the periodic gas phase composition. Becker et al. [17] used X-ray absorption spectroscopy to suggest that during lean-rich cycling a partially oxidized Pt surface is favorable for CH₄ dissociation and therefore has a higher apparent transient activity. They did not rule out the presence of a more reactive chemisorbed oxygen species. Enhancement by periodic operation occurs if the reaction rate dependence on the modulated variable has a convex dependence and the switching period τ_s is shorter than the response time of the catalyst, τ_c [18].

To illustrate, Fig. 12 shows the schematic dependence of the steady state CH₄ oxidation rate on the O₂ concentration, C_{O2}. The maximum at an intermediate C_{O2} defines two kinetic regimes, a positive-order (to the left) and negative-order (to the right). At the feed concentration given by $< C_{O2} >$ the rate is in the latter, inhibitory regime. Suppose now that C_{O2} is switched between the lower "rich" value C_{O2,r} and the higher "lean" value C_{O2,1} such that the average value is given by $< C_{O2} >$. Two limiting rates may be obtained depending on the magnitude of the switching period, given by τ_s . A second time constant of interest is the catalyst response time, τ_c . There are two limiting cases of interest; slow periodic modulation and fast periodic modulation, such

Fig. 12. Schematic showing dependence of $\rm CH_4$ oxidation rate on feed $\rm O_2$ concentration.

that for the former $\tau_s < < \tau_c$ and the latter $\tau_s > > \tau_c$.

The steady-state rate is the rate obtained when the feed concentration is constant in time. Thus at a steady feed concentration of < C_{O2} > the steady-state rate is given by $R_{SS}\{ < C_{O2} > \}$. On the other hand, for a slow periodic modulation ($\tau_s > > \tau_c$), the *cycleaverage rate* is the weighted-average rate:

$$R_{WA}\{ < C_{O2} > \} = d_r R\{C_{O2,r}\} + (1 - d_r) R\{C_{O2,l}\}$$
(4)

Here $< C_{O2} >$ is the cycle-average O₂ concentration given by

$$< C_{O2} > \{d_r\} = d_r C_{O2,r} + (1 - d_r) C_{O2,l}$$
 (5)

 d_r is the duty fraction of the rich feed. For example, for the case in which $d_r = 0.5$, then $< C_{O2} >$ is simply the arithmetic average of $C_{O2,r}$ and $C_{O2,l}$; i.e., $< C_{O2} > \{d_r = 0.5\} = (C_{O2,r} + C_{O2,l})/2$ and the cycle-average rate is the arithmetic average of $R\{C_{O2,r}\}$ and $R\{C_{O2,l}\}$. On the other hand, for fast periodic modulation ($\tau_s < < \tau_c$), the rate is given by a *pseudo steady-state rate* RPSS{ $< C_{O2} > \}$ that is given by the rate along the chord connecting the bounding intersection points. In this case the catalyst is unable to respond fast enough to the rapidly modulated feed and, as a result, a transient rate is obtained. Clearly, judiciously selected limiting values of C_{O2} can give a transient oxidation rate that exceeds the steady-state rate at the weighted average value O_2 concentration, $< C_{O2} >$.

For CH₄ oxidation, a modulated lean-rich feed induces a mixture of metallic and oxide states of Pt and Pd surface crystallites which provide sites for CH₄ adsorption and reaction. The spinel impact may be explained principally by its oxygen storage and release property. The $Mn_{0.5}Fe_{2.5}O_4$ spinel used in this study has a rather high oxygen storage capacity (OSC). Consider the following comparison in reduction of the spinel to that of conventional CeO₂ used in emission control catalysts:

R13:
$$Mn_{0.5}Fe_{2.5}O_4 + 3.5 H_2 \rightarrow 2.5 Fe + 0.5 MnO + 3.5 H_2O$$

R14:
$$CeO_2 + 0.5 H_2 \rightarrow 0.5 Ce_2O_3 + 0.5 H_2O$$

On a molar basis, $Mn_{0.5}Fe_{2.5}O_2$ stores about 7 times as much O as that of CeO₂. On a mass basis it stores 8.3 times as much. This high oxygen storage capacity of the MFO spinel is generated from the state transformation of Fe²⁺ and Fe³⁺ in the tetrahedral sites and Mn^{3+} and Mn^{4+} in the octahedral sites, producing oxygen vacancies under the transient lean/rich environment.

The role of the spinel during the lean-rich cycling is described as follows. During the rich phase of the cycle, the reduced spinel generates an oxygen vacancy. During the subsequent lean phase, oxygen vacancies are filled by oxygen supplied from dissociated O_2 . Subsequently, when the feed switches from lean to rich oxygen is released from the spinel to the PGM crystallites. An enhanced CH₄ oxidation performance is obtained by achieving a partially oxidized and metallic crystallites. As discussed earlier, metallic PGM crystallites are more active in the dissociative adsorption of CH₄ in the negative-order O_2 regime [16]. Further, Pt crystallites that are sustained through cycling in a more metallic state adsorb oxygen more weakly than the oxidized crystallites. Fouladvand et al. [19] suggested a reduction by ceria/zirconia in the possible deposition of a carbonaceous species during the rich phase.

In summary, enhancement of the CH_4 oxidation rate by modulation and spinel addition is a result of enhanced CH_4 activation on mixed metallic-oxidic PGM crystallites and the subsequent surface reaction with reactive oxygen provided from the spinel.

4. Conclusions

The oxidation performance of the PGM (Pt-Pd) + spinel (Mn_{0.5}Fe_{2.5}O₄) catalyst was investigated to quantify the effect of the spinel addition and of lean/rich feed modulation on the conversions of CH₄ and NO. A higher CH₄ oxidation rate was observed during modulation of a feed containing CH4 and oxygen, compared to the steadystate operation. More dramatic CH4 conversion enhancement was observed with an application-relevant feed simulating that of NG vehicle exhaust. Enhancement in the CH₄ conversion was accompanied by NO conversion enhancement. The role of spinel addition was also examined by comparing the catalytic performance of PGM + spinel, PGM-only and spinel-only materials. The spinel-only catalyst showed negligible CH₄ oxidation activity up to 600 °C. Moreover, under the steady-state conditions, the presence of spinel in the PGM catalyst was not beneficial to the catalytic performance. However, during modulation, both CH₄ and NO conversions were significantly enhanced by the presence of the spinel together with PGM. The beneficial promotional role of the spinel on the PGM-based catalyst is attributed to its effective oxygen storage and release property in maintaining the PGM in a favorable metallicoxidic state for CH4 activation and oxidation. The enhanced methane conversion in turn benefits the NO conversion. As methane conversion approaches completion so does the O₂ conversion given that the feed is slightly rich of stoichiometric. This creates a rich environment conducive for the reaction of NO with CH4 and its partial oxidation products H₂ and CO. Finally, the study shows convincing data that the combination of the spinel and modulation may reduce the precious metal loading required to achieve a high CH₄ oxidation conversion.

CRediT authorship contribution statement

Sung Bong Kang: Conceptualization, Methodology, Investigation, Writing - original draft. Kyle Karinshak: Conceptualization, Methodology, Investigation, Validation, Writing - original draft, Writing - review & editing. Pak Wing Chen: Methodology, Investigation. Stephen Golden: Conceptualization, Methodology, Writing - review & editing. Michael P. Harold: Conceptualization, Methodology, Investigation, Writing - original draft, Writing - review & editing, Supervision, Project administration, Resources, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

- [1] R.W. Howarth, R. Santoro, A. Ingaffea, Clim. Change 106 (2011) 679-690.
- [2] P. Gélin, M. Primet, Appl. Catal. B 39 (2002) 1-37.
- [3] H.S. Gandhi, G.W. Graham, R.W. McCabe, J. Catal. 216 (2003) 433-442.
- [4] G. Beulertz, M. Votsmeier, R. Moos, Appl. Catal. B 165 (2015) 369-377.
- [5] J. Kašpar, P. Fornasiero, M. Graziani, Catal. Today 50 (1999) 285–298.
- [6] P.S. Lambrou, C.N. Costa, S.Y. Christou, A.M. Efstathiou, Appl. Catal. B 54 (2004) 237–250.
- [7] X. Xie, Y. Li, Z.-Q. Liu, M. Haruta, W. Shen, Nature 458 (2009) 746–749.
- [8] P. Silveston, Catal. Today 25 (1995) 175–195.

[9] H. Muraki, K. Yokota, Y. Fujitani, Appl. Catalysis B: Environ. 48 (1988) 93–105.
[10] J.H.B.J. Hoebink, A.J.L. Nievergeld, G. Marin, Chem. Eng. Sci. 54 (1999)

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- 4459–4468.
- [11] P. Koci, M. Kubicek, M. Marek, Catal. Today 98 (2004) 345-355.
- [12] N. Macleod, R.M. Lambert, Appl. Catal. B 35 (2002) 269-279.
- [13] S.H. Oh, P.J. Mitchell, R.M. Siewert, J. Catal. 132 (1991) 287–301.
 [14] G.S. Bugosh, V.G. Easterling, I.A. Rusakov, M.P. Harold, Appl. Catal. B 165 (2015) 68–78.
- [15] R. Burch, P.K. Loader, Appl. Catal. B 15 (1994) 149–164.
 [16] Y.H. Chin, C. Buda, M. Neurock, E. Iglesia, J. Am. Soc. Brew. Chem. 133 (2011)
- 15958–15978.[17] E. Becker, P.-A. Carlsson, L. Kylhammar, M. Newton, M. Skoglundh, J. Phys. Chem.
- [17] E. Becker, P.-A. Carisson, L. Kymanimar, M. Newton, M. Skogiunun, J. Phys. Chem. C 115 (2010) 944–951.
- [18] G. Marin, Personal Communication (2019).
- [19] S. Fouladvand, M. Skoglundh, P.-A. Carlsson, Chem. Eng. J. 292 (2016) 321-325.