Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supplementary Information

Section 1. Performance comparison of spinel and ceria-zirconia as oxygen storage material

The use of the $Mn_{0.5}Fe_{2.5}O_4$ (MFO) spinel and the more commonly used ceria-zirconia (CZO) as the oxygen storage material (OSM) in the PGM monolith catalysts is compared with the same OSM loading. The composition $Ce_{0.3}Zr_{0.7}O_2$ was chosen as to represent CZO in this study. The CH_4 conversion profiles under the modulated and time-invariant feed conditions over the PGM+Spinel and PGM+CZO catalysts were shown in Fig. S1a. The estimated O_2 concentration profiles were shown in Fig. S1b. The method of estimating the O_2 concentration profile is explained in the next section. In addition, the steam reforming of CH_4 (SRM) performance of the PGM+CZO catalyst is compared with that of the PGM+Spinel catalyst (Fig. S1c).

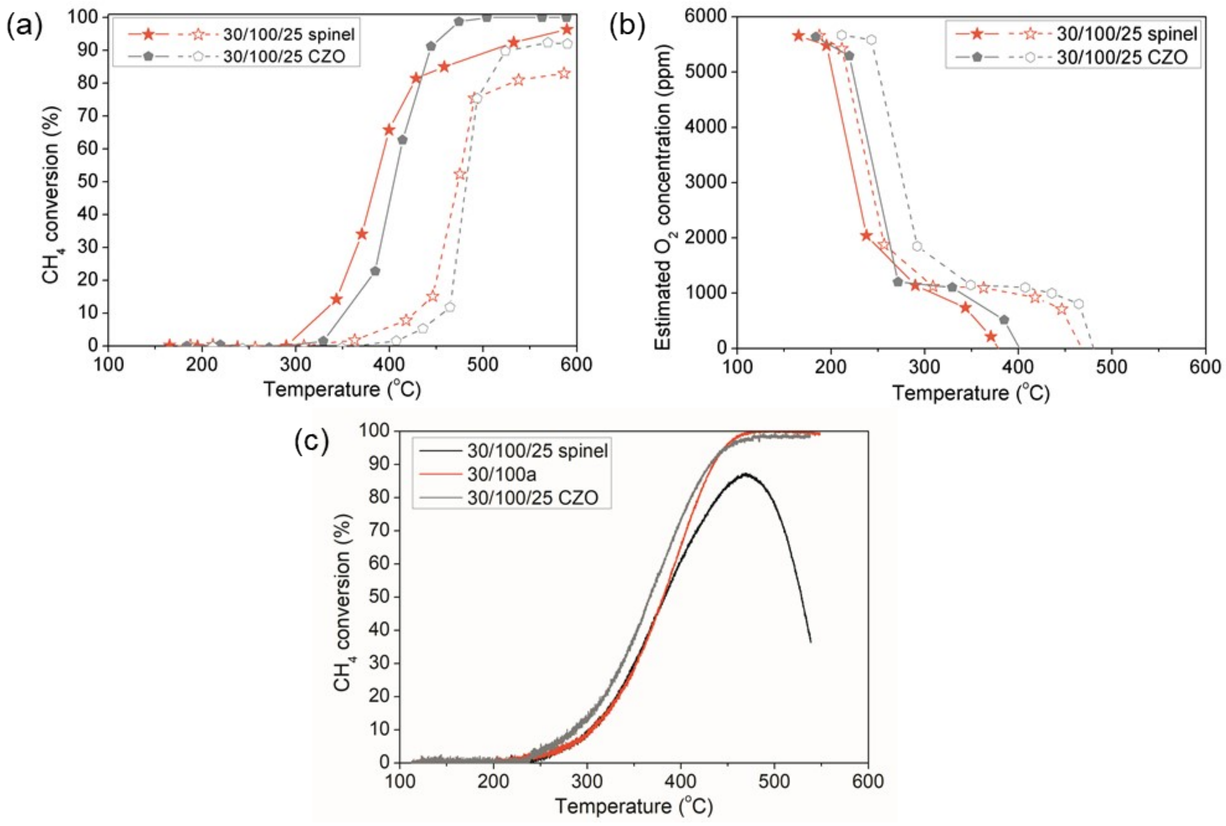

Fig. S1. (a) CH_4 conversion for modulated [filled symbols] and time-invariant feed [unfilled symbols] over PGM+Spinel and PGM+CZO catalysts; **(b)** estimated O_2 profiles for modulated [filled symbols] and time-invariant [unfilled symbols] feed; **(c)** steam reforming performance of PGM+Spinel, PGM-Only and PGM+CZO catalysts.

Section 2. Estimation of effluent O_2 concentration profile

The effluent O_2 concentration profile was used to denote the transition from the aerobic to the anaerobic regime of CH_4 reaction chemistries. After O_2 depletion, CH_4 steam reforming contributes to the CH_4 conversion. In the flow experiment study, a mass spectrometry was used to measure H_2 and O_2 concentrations. However, the measured O_2 concentration values were not accurate due to the false positive signal of O_2 contributed by the presence of water in the feed. Before measuring O_2, the background was first taken in the presence of 10% H_2O, then O_2 calibration was conducted also in the presence of 10% H_2O. This approach did not guarantee accurate O_2 measurement since the H_2O concentration was not constant throughout the experiment due to the reactions or fluctuation in the vapor feed system. In order to circumvent this issue, the effluent O_2 concentration profiles were estimated instead. In this section, the method used to calculate the O_2 concentration is discussed in detail.

The effluent O_2 concentration profiles were estimated based on the conversions of CH_4, CO, H_2, and the formation of NO_2 (eqn S1 to S4). No CO and H_2 formation were observed until at temperature above 400°C (modulated feed) and above 470°C (time-invaraint feed) for both PGM-Only (30/60a) and PGM+Spinel (30/60/15) catalysts. Thus, CH_4 partial oxidation is not considered to be a pathway for CH_4 oxidation and only CH_4 full oxidation is considered.

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad \text{eqn (S1)}$$

$$H_2 + 0.5O_2 \rightarrow H_2O \qquad \text{eqn (S2)}$$

$$CO + 0.5O_2 \rightarrow CO_2 \qquad \text{eqn (S3)}$$

$$NO + 0.5O_2 \leftrightarrow NO_2 \qquad \text{eqn (S4)}$$

Specifically, formation of NH_3 and N_2O were detected under the full feed conditions. The NH_3 formation originates from the NO reduction by H_2 (eqn S5). The formation of N_2O can come from the reduction of NO by H_2 (eqn S6) and CO (eqn S7). Thus, part of the H_2

and CO conversion came from oxidation reactions with NO. For O_2 concentration calculation, N_2O formation was assumed to occur via eqn S6 only.

$$NO + 2.5H_2 \rightarrow NH_3 + H_2O \qquad \text{eqn (S5)}$$

$$NO + 0.5H_2 \rightarrow 0.5N_2O + 0.5H_2O \qquad \text{eqn (S6)}$$

$$NO + 0.5CO \rightarrow 0.5N_2O + 0.5CO_2 \qquad \text{eqn (S7)}$$

To summarize, a few assumptions were made for the O_2 concentration estimation:

1. CH_4 oxidation occurs via full oxidation.

2. The H_2 and CO formations at high temperatures come from CH_4 steam reforming.

3. The NH_3 and N_2O formations come from NO reduction with the H_2 fed before full H_2 consumptions. After the full conversion of H_2, the NH_3 and N_2O formations come from NO reduction with the H_2 formed from CH_4 steam reforming.

While the exact measured O_2 values were not accurate, the slope changes in the profile were used as a reference. In other words, the slope changes in the estimated O_2 profile should be similar such that the estimated O_2 consumption is close to the actual profile. The method of O_2 calculation was demonstrated at the third temperature point (227ºC) for the PGM+Spinel (30/60/15) catalyst under both time-invariant and modulated feed conditions. The NO_2, NH_3 and N_2O formation profiles were shown in Fig. S2a and S2b. The specific concentration values of all the species at 227ºC were listed in table S2.

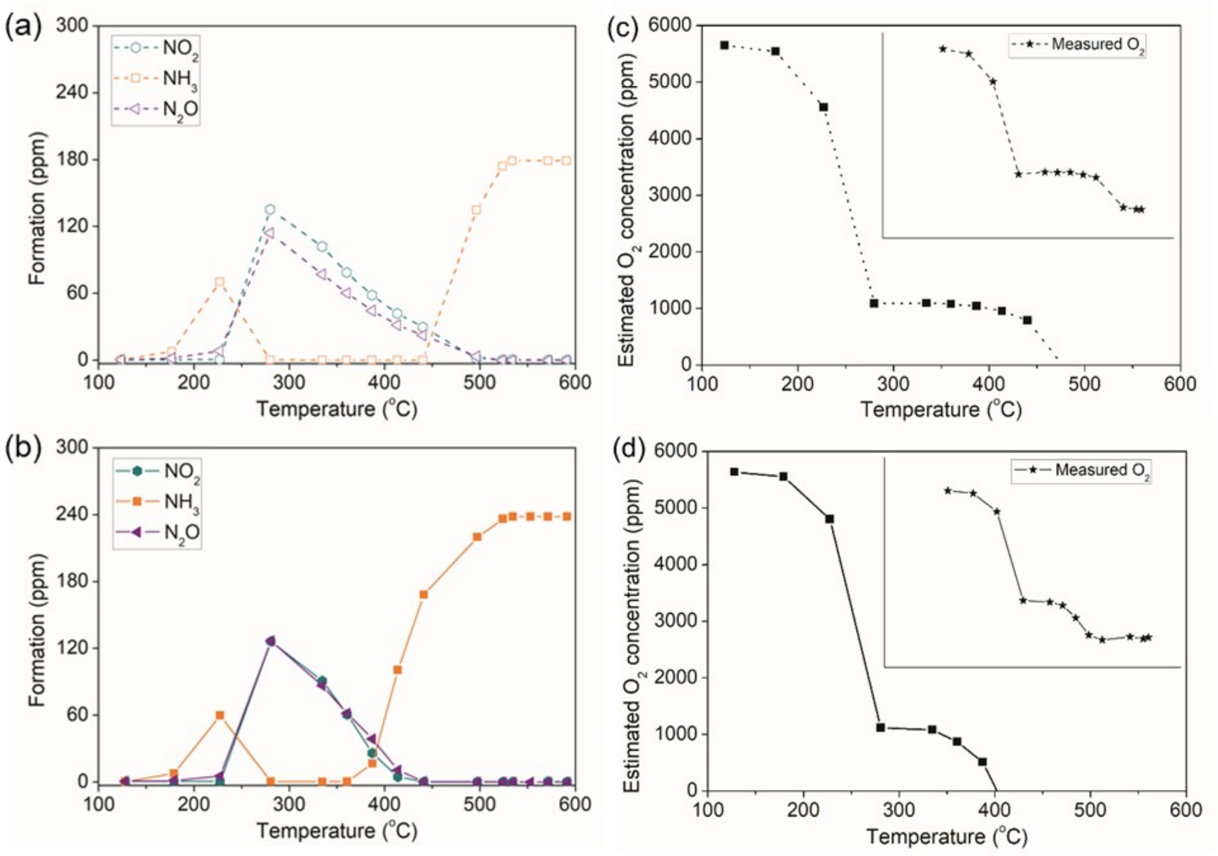

Fig. S2. **(a)** NO_2, NH_3, N_2O formations under time-invariant feed [unfilled symbols] and **(b)** under modulated feed [filled symbols] over PGM+Spinel (30/60/15) catalyst; **(c)** estimated O_2 concentration profile under time-invariant feed and **(d)** under modulated feed over PGM+Spinel (30/60/15) catalyst (top right refers to measured O_2 concentration profiles for comparison).

Table S1. Measured concentration values at 227ºC under both time-invariant and modulated feed conditions for PGM+Spinel (30/60/15) catalyst.

Species	Time-invariant feed	Modulated feed
H_2	288 ppm (71% conversion)	336 ppm (66% conversion)
CO	6382 ppm (20% conversion)	6823 ppm (15% conversion)
CH_4	1491 ppm (1% conversion)	1500 ppm (0% conversion)

NO	892 ppm (11% conversion)	917 ppm (8% conversion)
NO_2	1 ppm	0 ppm
NH_3	70 ppm	60 ppm
N_2O	8 ppm	5 ppm
H_2 used for NH_3 and N_2O formation	180 ppm (18% of H_2 fed)	152 ppm (15% of H_2 fed)

The O_2 concentration was calculated based on the following equation:

$$O_{2,cal} = O_{2,fed} - O_2\ used\ for\ NO_2\ formation - O_2\ used\ for\ CO\ oxidation - O_2\ used\ fo$$
$$oxidation - O_2\ used\ for\ H_2\ oxidation$$

eqn (S8)

For instance, under time-invariant feed, the calculated O_2 concentration is:

$$O_{2,cal} = 5650 - (1 * 0.5) - (0.01 * 20 * 8000 * 0.5) - (0.01 * 1 * 1500 * 2) -$$
$$+ (0.01 * 18 * 1000 * 0.5) = 4555\ ppm$$

The last addition term came from the assumption that 18% of H_2 fed was used for NO reduction instead of oxidation.

Similarly, the calculated O_2 concentrations under modulated feed are:

$$O_{2,cal}(lean) = 7900 - (0 * 0.5) - (0.01 * 15 * 8000 * 0.5) - (0.01 * 0 * 1500 * 2) -$$
$$+ (0.01 * 15 * 1000 * 0.5) = 7045\ ppm$$

$$O_{2,cal}(rich) = 3400 - (0 * 0.5) - (0.01 * 15 * 8000 * 0.5) - (0.01 * 0 * 1500 * 2) -$$
$$+ (0.01 * 15 * 1000 * 0.5) = 2545\ ppm$$

$$O_{2,cal}(avg) = (7045 + 2545)/2 = 4795\ ppm$$

The average estimated O_2 concentration over the lean and rich cycle is 4795 ppm.

Using the method demonstrated above, the O_2 values were calculated for all the temperature points, which were shown in Fig. S2c and S2d. The estimated O_2 profiles have similar slopes compared to the measured O_2 profiles shown in the upper corner of the figures.

Section 3. Repeated CH_4 steam reforming experiment

Repeated steam reforming experiment was conducted on the PGM+Spinel (30/100/25) catalyst. After the first experiment was completed, the catalyst was cooled to ~115ºC in the presence of 3% O_2/N_2 then purge with N_2 only for 15 min before the second experiment was started. No CO or CO_2 species was detected during the oxidizing cooling step. As shown in Fig. S3, similar CH_4 conversion profile was obtained in the second run as compared to the profile shown in Fig. 6. The CH_4 conversion reached a maximum value at ~50% but subsequently dropped to ~3% conversion.

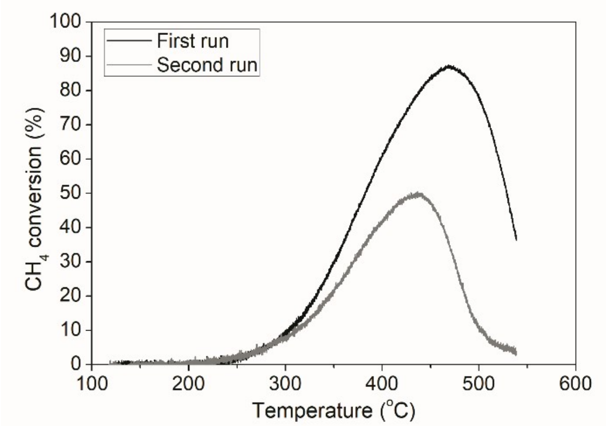

Fig. S3. CH_4 conversion under two steam reforming runs over PGM+Spinel (30/100/25) catalyst [cooling condition after first run: 3% O_2/N_2]

Section 4. Adsorption behavior of MnO_xH_y on Pt(211)

Adsorption behavior of MnO_xH_y species on step site of Pt(211) was evaluated to probe the ease of Pt encapsulation by Mn oxides and hydroxides. Adsorption of MnO monomers on Pt(211) steps was found to be endothermic. The favorable adsorption of MnOH monomers on Pt(211) and when embedded in Pt(211) shows possibility of Pt site blocking by MnO_xH_y species.

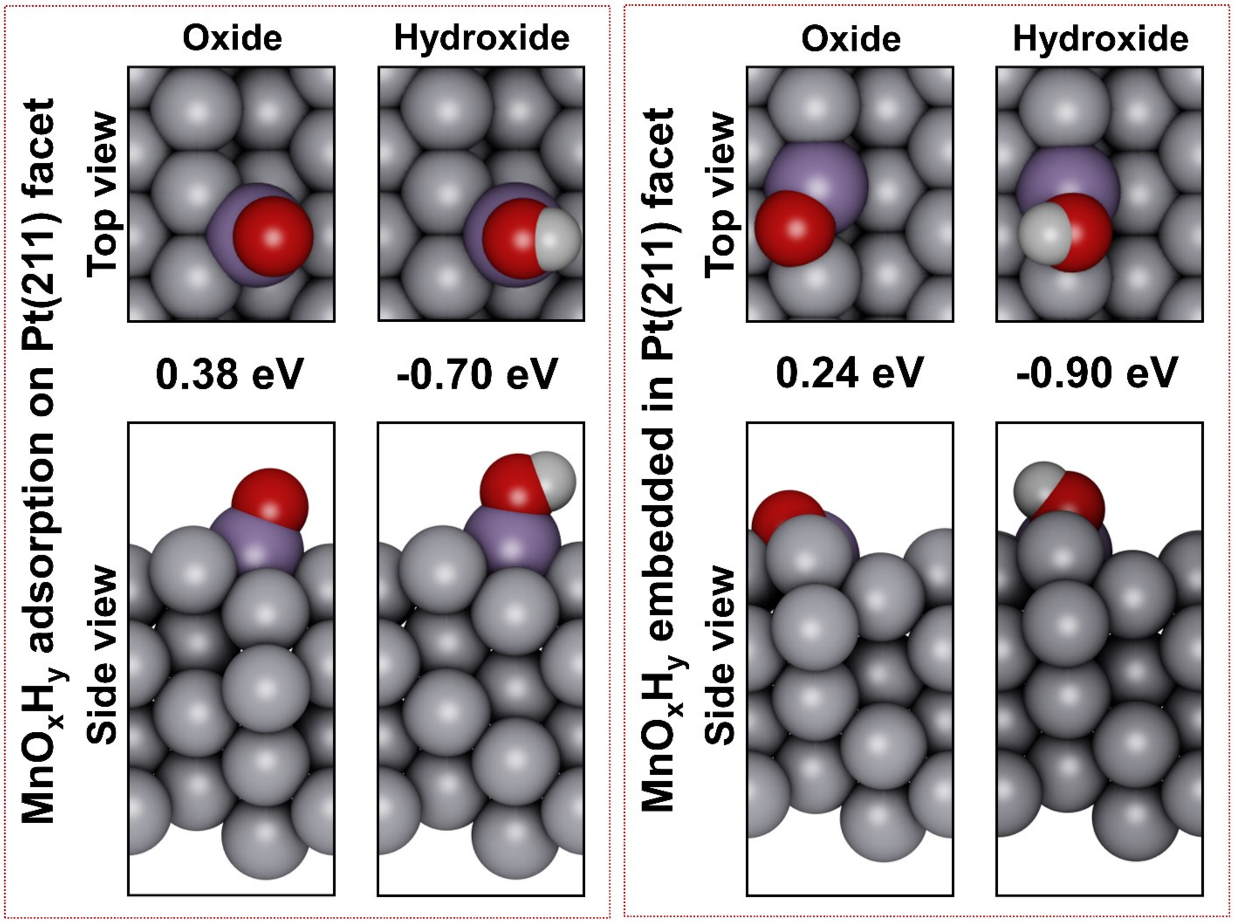

Fig. S4. Left panel: Energy of adsorption of MnO_xH_y monomers on the step site of Pt(211). Right panel: Energy for embedding MnO_xH_y monomers in Pt(211) steps.

Section 5. Estimated effluent O_2 profile of the zoned catalysts

As discussed in section 1, the same approach was used to obtain the estimated O_2 profile of the zoned catalysts under both time-invariant and modulated feed conditions, as shown in Fig. S5.

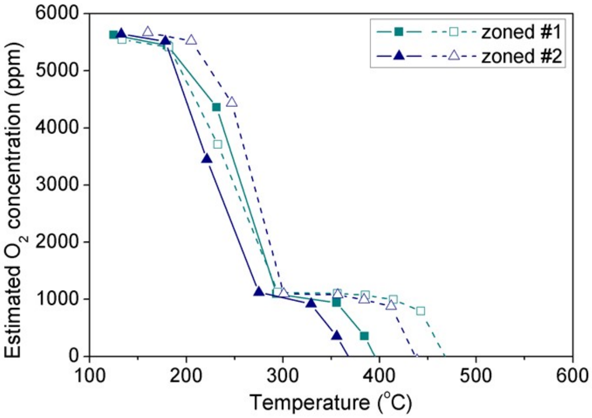

Fig. S5. Estimated O_2 effluent concentration of the zoned catalysts under time-invariant [unfilled symbols] and modulated feeds [filled symbols]

Section 6. Normalized DRIFTS spectra of the PGM-Only and PGM+Spinel catalysts

The CO-DRIFTS experiments were carried out to obtain semi-quantitative information such as peak area loss. The CO peak area loss before and after steam reforming could be quantified from the normalized spectra. However, the obtained area values would largely depend on the chosen wavenumber range and the baseline correction method. Thus, the quantification based on DRIFTS data on different samples are not conclusive. Nevertheless, the normalized spectra can be used to obtain some useful information. In this section, normalized spectra based on different wavenumber ranges, of samples treated with different experimental conditions were provided and compared.

The measured transmittance I were normalized based on the following equation:

$$Normalized\ I = \frac{(I - I_{min})}{(I_{max} - I_{min})}$$

The I_{min} and I_{max} represent the minimum and maximum measured transmittance within a range of wavenumber. For example, in Fig. S6.1a, the spectra of the fresh PGM-Only and fresh PGM+Spinel were normalized in the wavenumber range of 1150 to 3700 cm^{-1} and in Fig. S6.1b, the spectra were normalized in the wavenumber range of 1970 to 2110 cm^{-1}. Normalized spectra based on different wavenumber ranges were provided in Fig. S6.2 ~ S6.4 as well.

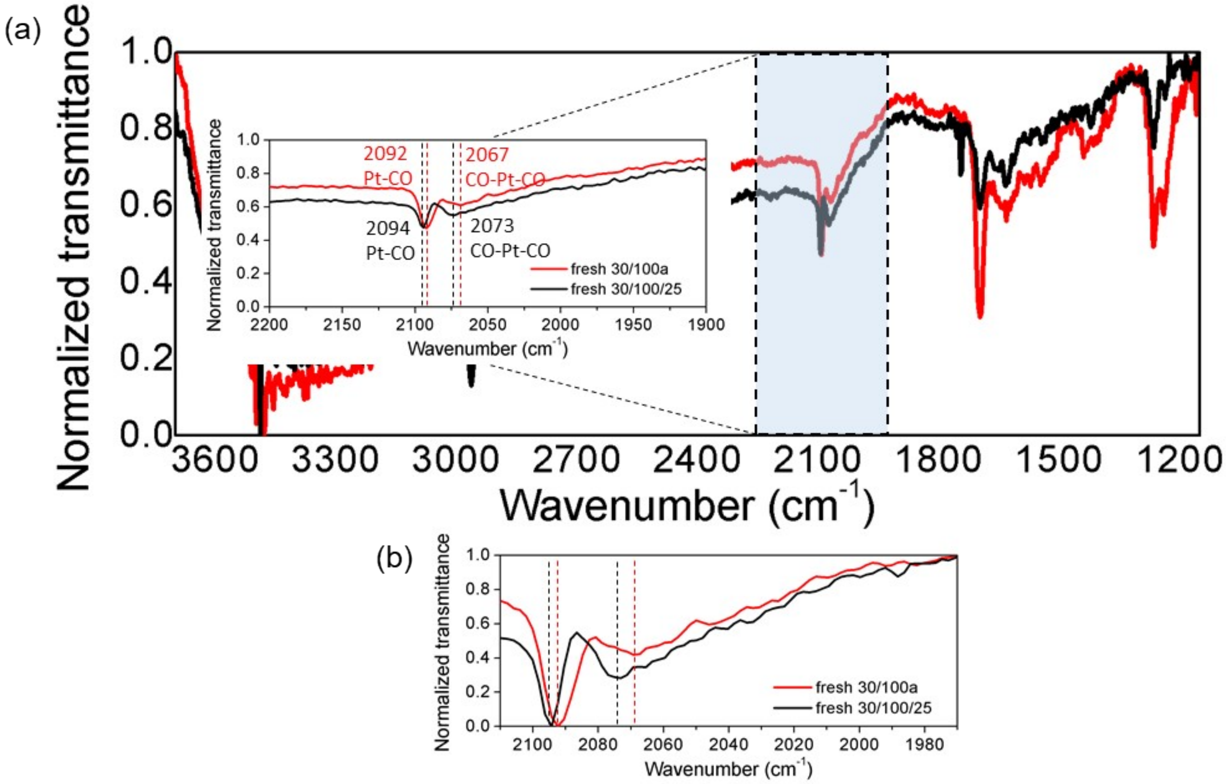

Fig. S6. 1. (a) Normalized DRIFTS spectra of fresh PGM-Only and PGM+Spinel catalyst in normalized wavenumber range of 1150 to 3700 cm^{-1} and **(b)** in normalized wavenumber range of wavenumber range of 1970 to 2110 cm^{-1}

As shown in Figs. S6.1a and S6.1b, the CO adsorption peaks on Pt are similar for both fresh PGM-Only and fresh PGM+Spinel catalyst. This suggests that adding spinel to the PGM-Only catalyst has a negligible impact on the CO adsorption on Pt.

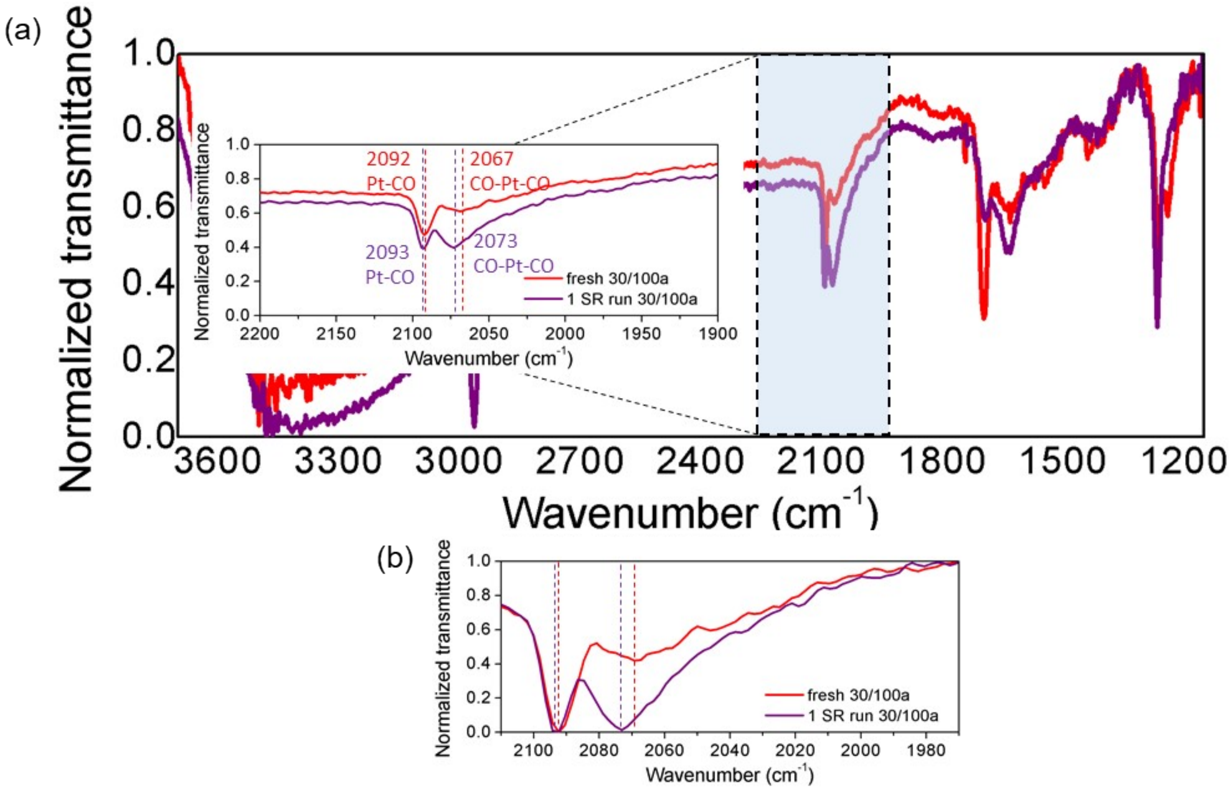

Fig. S6. 2. (a) Normalized DRIFTS spectra of fresh PGM-Only and post-1 SR run PGM-Only catalyst in normalized wavenumber range of 1150 to 3700 cm^{-1} and **(b)** in normalized wavenumber range of 1970 to 2110 cm^{-1}

After 1 steam reforming run, the intensity of the CO-Pt-CO peak increases for the PGM-Only catalyst as shown in Figs. S6.2a and S6.2b. This may suggest more Pt site for CO co-adsorption is available after reaction.

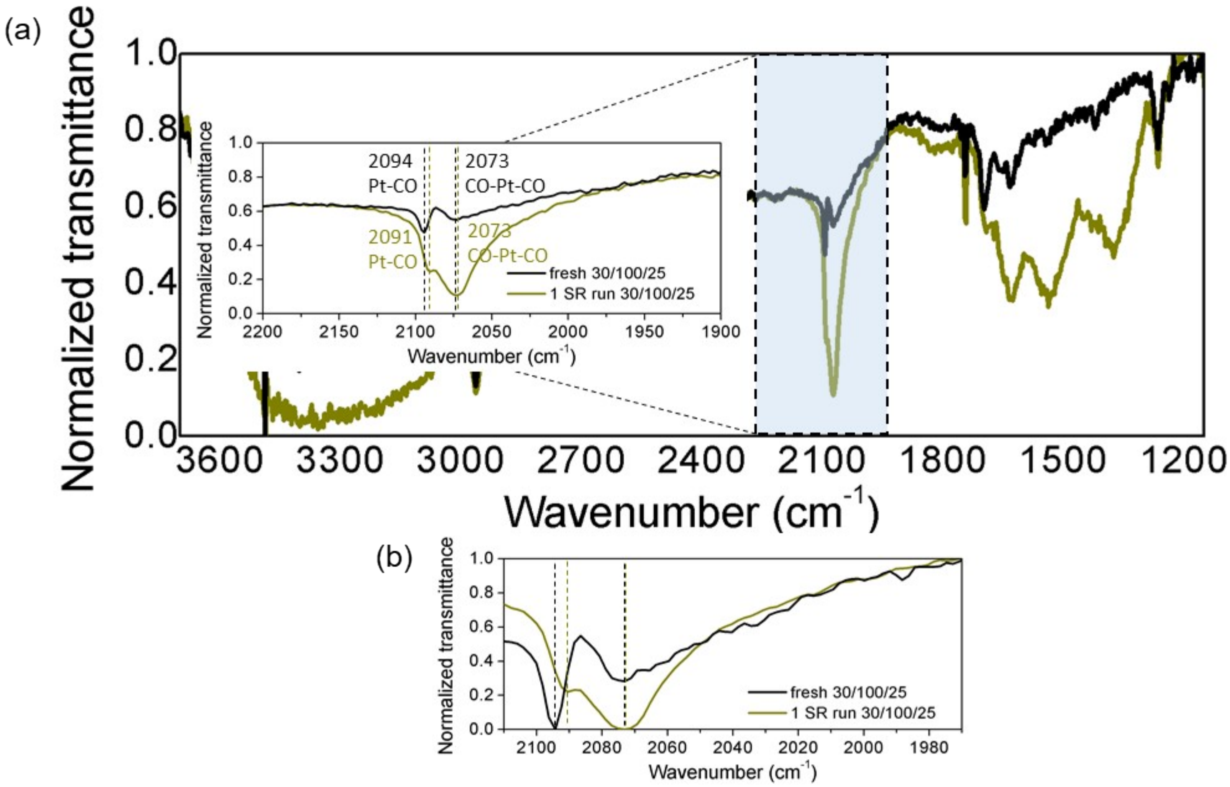

Fig. S6. 3. (a) Normalized DRIFTS spectra of fresh PGM+Spinel and post-1 SR run PGM+Spinel catalyst in normalized wavenumber range of 1150 to 3700 cm^{-1} and **(b)** in normalized wavenumber range of 1970 to 2110 cm^{-1}

Similar data for the PGM+Spinel catalyst in Figs. S6.3a and S6.3b reveal that CO prefer to co-adsorb on Pt after 1 steam reforming run, as illustrated by the change in dominant CO adsorption peak from CO-Pt to CO-Pt-CO. The change in the CO adsorption behavior may be altered by the interaction between migrated base metal species and Pt site, or the sintering of particular Pt site. However, these possibilities can not be validated without more in-depth surface characterization and thus, not explored further in the current study.

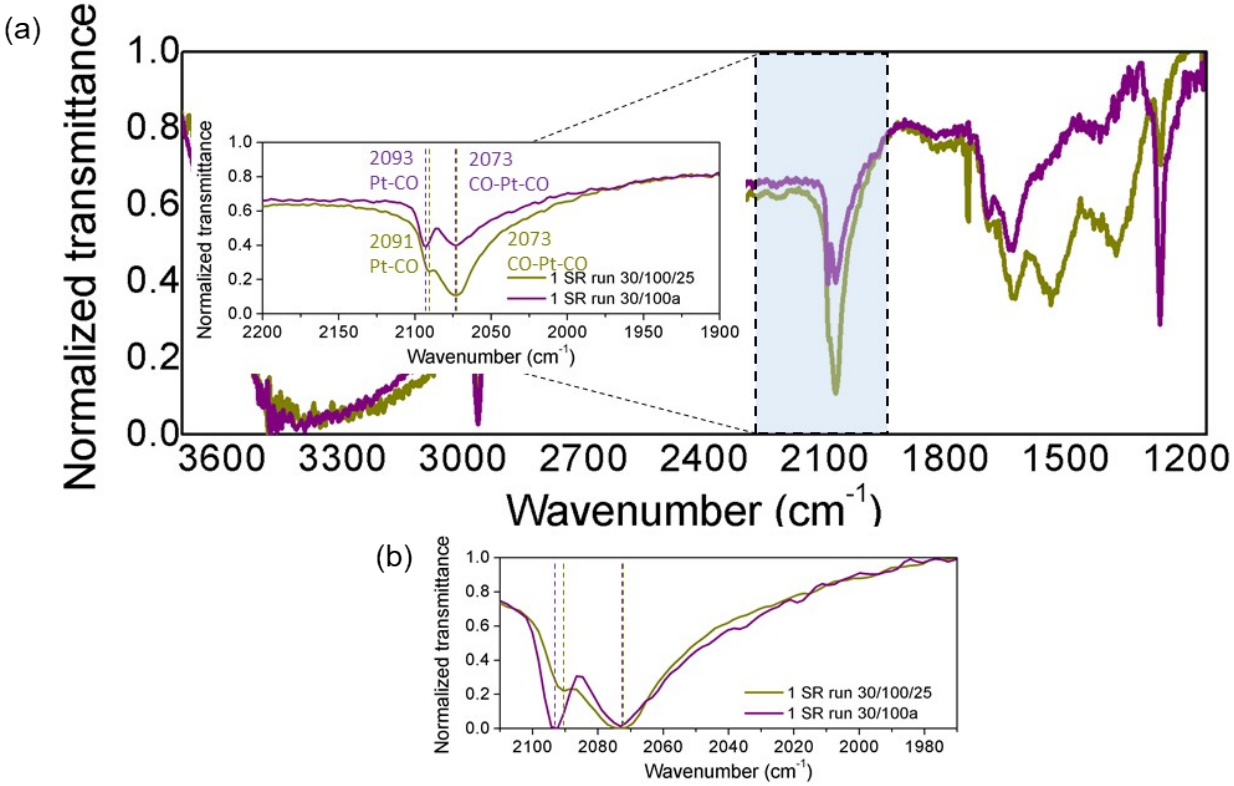

Fig. S6. 4. (a) Normalized DRIFTS spectra of post-1 SR run PGM-Only and post-1 SR run PGM+Spinel catalyst in normalized wavenumber range of 1150 to 3700 cm^{-1} and **(b)** in normalized wavenumber range of 1970 to 2110 cm^{-1}

The normalized spectra of the PGM-Only and PGM+Spinel samples after one SR treatment are compared in Figs. S6.4a and S6.4b. As discussed above, different CO adsorption features on Pt sites were observed for the PGM-Only and PGM+Spinel samples after one SR treatment. The alteration in CO adsorption behavior due to possible site changes induced by the steam reforming reaction, Pt sintering or interaction from the migrated base metal species are out of the scope of the current study and thus, are not further discussed here.

Section 7. Effect of overall spinel loading on catalyst performance

The correlation of T_{50} values and the overall spinel loading of the catalyst is shown in Figs. S7a and S7b. Under both modulated and time-invariant feed conditions, PGM+Spinel (30/140/35) catalyst, which has a higher spinel loading of 35 g/L compared to the other two catalysts (30/100/25, 30/60/15), gives the lowest T_{50} values. The performance improvement of the zoned catalyst #2 is therefore, explained by its high spinel loading in the front oxidation zone.

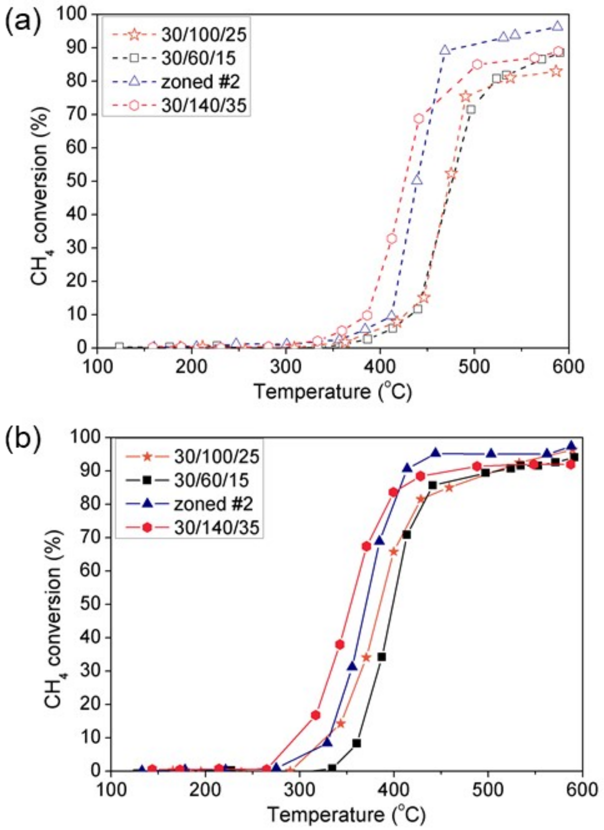

Fig. S7. CH_4 conversion profiles of PGM+Spinel catalysts (30/140/35, 30/100/25, 30/60/15) and zoned catalyst #2 under **(a)** time-invariant feed [unfilled symbols] and **(b)** under modulated feed [filled symbols]