

## Electronic Supporting Information:

# Strategy to eliminate catalyst hot-spots in the partial oxidation of methane: enhancing catalyst activity for direct hydrogen production in the oxidation of methane by reducing the reactivity of lattice oxygen

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## Experimental Section

Rare earth oxides were prepared by a hydrothermal method.<sup>1</sup> Mn<sub>3</sub>O<sub>4</sub> (SP) was purchased (Sinopharm Chemical Reagent Co. Ltd.).

The catalytic activity testing of catalyst for the methane oxidation was performed in a fix-bed reactor at atmospheric pressure, and the pressure drop through the catalyst bed may be negligible. Typically, 0.1 g catalyst was packed in the quartz tubular reactor, and type-K thermocouple was adopted to monitor the bed temperature of catalyst. The reactant gas consisted of 0.8% (vol.) CH<sub>4</sub>, 21% O<sub>2</sub> and 78.2% Ar, and GHSV was 60000 mL h<sup>-1</sup> g<sup>-1</sup>. The effluent gas was analyzed by gas chromatograph (GC 9750, FULI Co. Ltd) and on-line quadrupole mass spectrometer (MS, IPC 400, INFICON Co. Ltd.).

The reactant gas consisted of 0.8 % CH<sub>4</sub>, 21% CO<sub>2</sub> and 78.2% Ar in the CO<sub>2</sub> reforming. In the methane steam reforming, the reactant gas consisted of 0.8% CH<sub>4</sub> and Ar, and this mixture gas passed through ice water bath to carry steam into reactor. Both GC and MS were used to monitor the effluent gas. The operating procedures were similar to the catalytic oxidation of methane.

In the methane pulse experiments, 0.1 g catalyst was packed in the middle of U-shaped quartz tubular reactor, and was degassed at 750°C for 3 h in He (30 mL min<sup>-1</sup>, 99.999%). After the temperature was cooled down to 650°C, 77 μL 10%CH<sub>4</sub>/Ar was pulsed into the reactor at the frequency of 0.0083 Hz. The effluent gas was monitored by MS.

The *in-situ* DRIFTS experiment was performed on a Nicolet NEXUS 670. The catalyst was degassed in He (30 mL min<sup>-1</sup>, 99.999%) at 600°C for 3 h. After the temperature was cooled down to 500°C, the background spectrum was collected in He, and then methane was introduced into the reactor. After methane swept through reactor at 500°C for 30 min, the system is flushed by He, and the IR spectrum was collected, and then this spectrum deducted the background spectrum to get the spectra of Figure 3.

In the testing of TPR, 0.1 g catalyst was used, the heating rate is 10°C min<sup>-1</sup>, and on-line MS was used as the detector. The catalyst was pretreated at 750°C for 3 h in Ar. After the reactor was cooled down to room temperature, 8% H<sub>2</sub>/Ar (or CH<sub>4</sub>/Ar) of 70 mL min<sup>-1</sup> was introduced into the reactor instead of Ar.

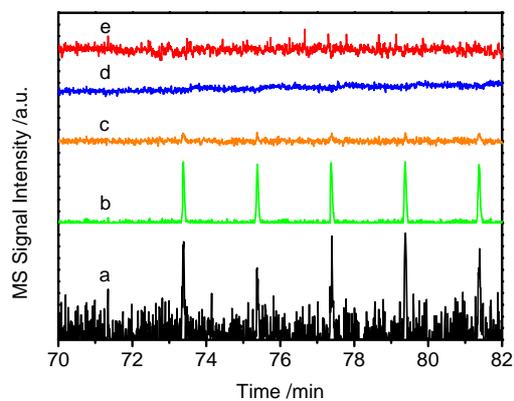
**Table S1.** Hydrogen yield in the oxidation of methane on different rare earth oxides <sup>[a]</sup>

Oxide catalyst	Eu	Gd	Tb	Dy	Ho	Tm	Yb	Lu	Y
Temperature /°C <sup>[b]</sup>	601	582	613	753	593	596	599	671	586
Conversion of methane /% <sup>[c]</sup>	53.6	32.4	38.9	60.9	31.2	37.4	28.9	33.4	46.1
Maximum yield of H <sub>2</sub> /%	11.5	9.8	9.6	2.3	9.8	8.5	7.2	6.1	11.5

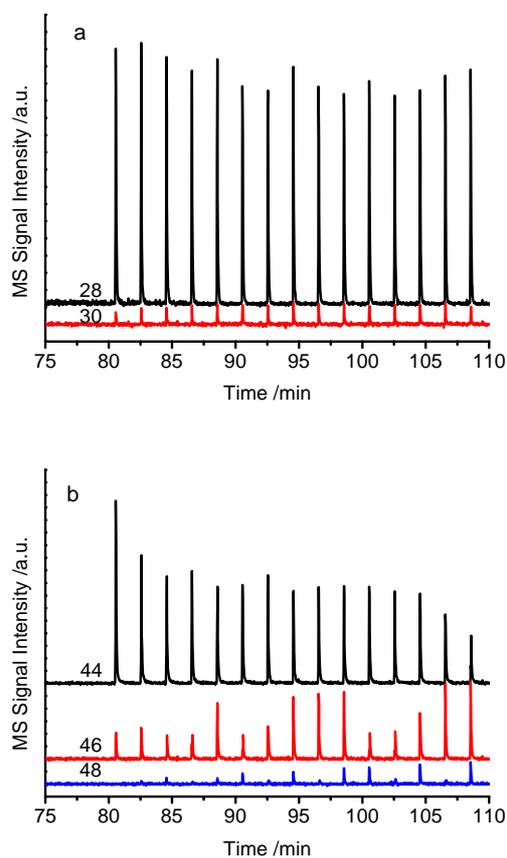
<sup>[a]</sup> The reactant gas consisted of 0.8% CH<sub>4</sub>, 21% O<sub>2</sub>, and 78.2% Ar, and the GHSV was 60000 mL h<sup>-1</sup> g<sup>-1</sup>. The catalyst was packed in the quartz tubular reactor, and the products were analyzed by gas chromatograph equipped with a TCD detector;

<sup>[b]</sup> The reaction temperature in the maximum hydrogen yield;

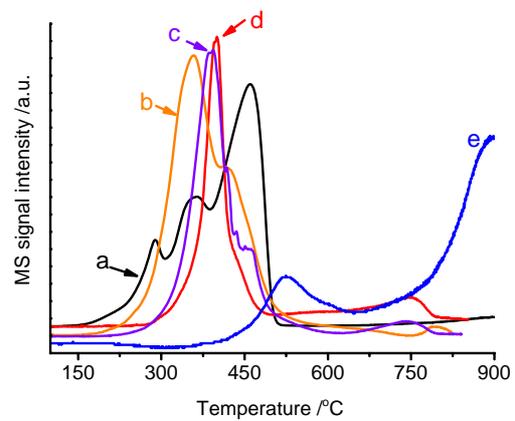
<sup>[c]</sup> The methane conversion in the maximum hydrogen yield.



**Figure. S1.** MS signals of (a) methane and (b) CO<sub>2</sub>, (c) CO, (d) H<sub>2</sub>O, and (e) H<sub>2</sub> over Mn<sub>3</sub>O<sub>4</sub> in the CH<sub>4</sub> pulse experiment at 650°C.



**Figure. S2.** MS signals of (a) CO ( $m/z=28, 30$ ) and (b) CO<sub>2</sub> ( $m/z=44, 46, 48$ ) in isotopic oxygen tracer experiment with mixture of <sup>18</sup>O<sub>2</sub> and CH<sub>4</sub> on Er<sub>2</sub>O<sub>3</sub> at 650 °C. Water was not measured because the MS signal of water with <sup>18</sup>O is not trustable. [2]



**Figure. S3.** H<sub>2</sub>-TPR profiles of Mn-Er-O catalysts with the Mn/Er atom ratio of (a) 1/0, (b) 9/1, (c) 5/5, (d) 1/9, and (e) 0/1.

1. X. Wang, X. M. Sun, D. P. Yu, B. S. Zou and Y. D. Li, *Adv. Mater.*, 2003, 15, 1442-1445.