Supporting Information

Consequence of products from oxidative coupling of methane in non-oxidative high temperature environment

*Haruka Komada, [a] Keisuke Obata, [a] Duanxing Li, [a] S. Mani Sarathy, [b,c] and Kazuhiro Takanabe *, [a, d]*

[a] Department of Chemical System Engineering, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo, Japan

[b] Clean Combustion Research Center (CCRC), Physical Sciences and Engineering Division, King Abdullah University of Science and Technology (KAUST), Thuwal, 23955-6900, Saudi Arabia.

[c] KAUST Catalysis Center (KCC), Physical Sciences and Engineering Division, King Abdullah University of Science and Technology (KAUST), Thuwal, 23955-6900, Saudi Arabia.

[b] PRESTO, Japan Science and Technology Agency (JST), Kawaguchi, Saitama, Japan
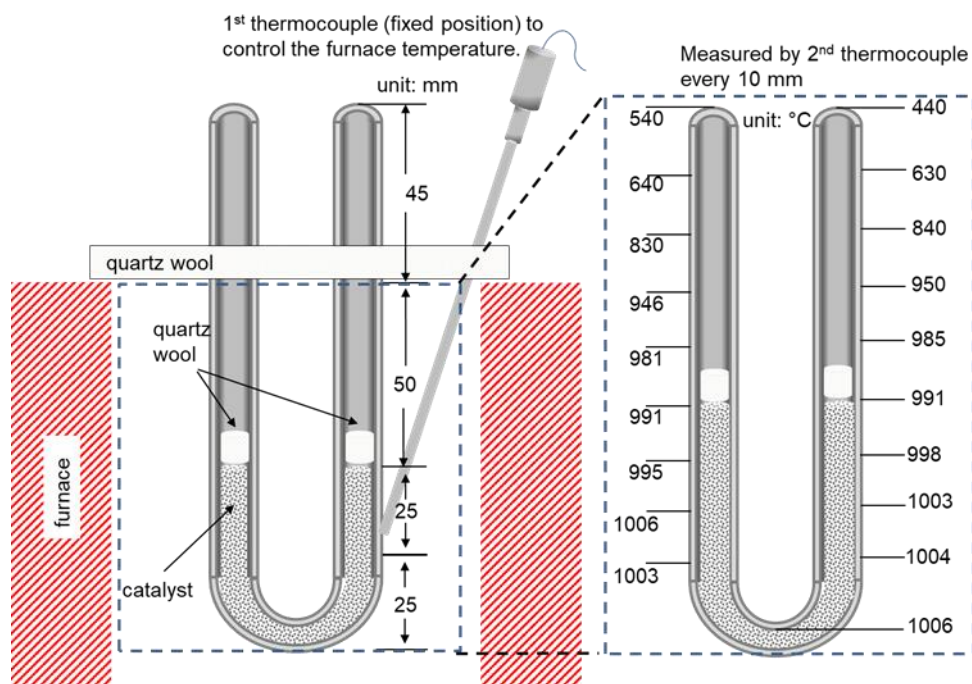
Figure S1. Temperature distribution along the U-shaped quartz reactor measured by 2nd thermocouple while the furnace temperature was maintained at 1000 °C. The catalyst bed was filled with 760 mg of 5 wt% Na_2WO_4/SiO_2. Inlet gas: CH_4 10 kPa, O_2 1.7 kPa, H_2O 1.7 kPa, total pressure 101 kPa, Ar balance, 80 mL min^{-1}.
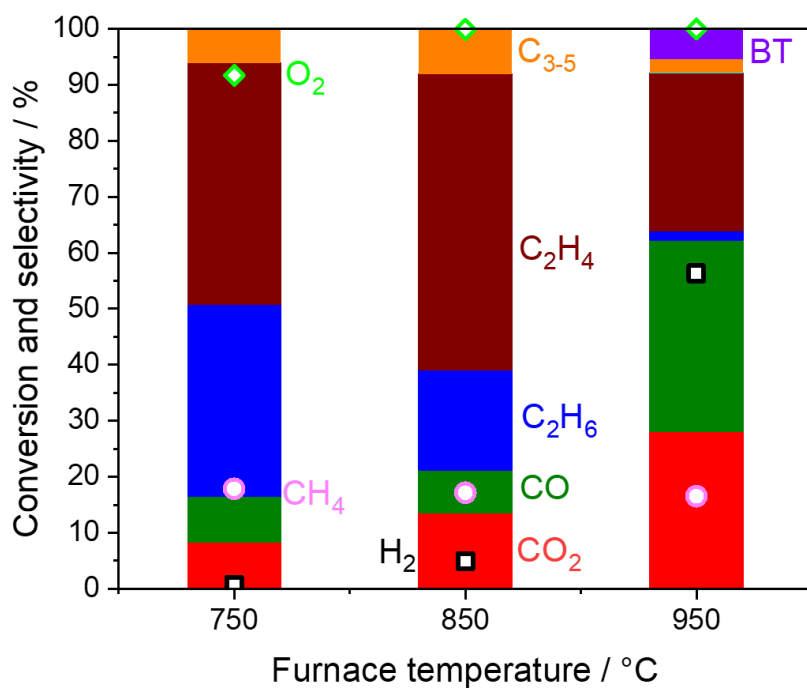
Figure S2. Product distribution and conversions of CH_4 and O_2 from the outlets the first reactor filled with 800 mg of 5 wt% Na_2WO_4/SiO_2 at 750, 850, and 950 °C. Inlet gas; CH_4 10 kPa, O_2 1.4 kPa, H_2O 1.7 kPa, total pressure 101 kPa, Ar balance, 40 mL min^{-1}.
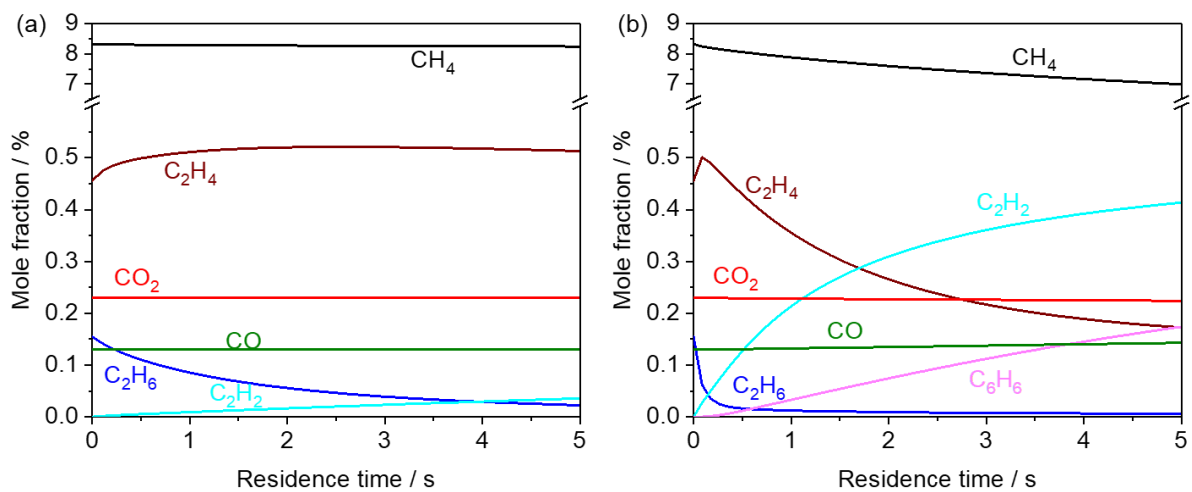
Figure S3. Simulated mole fractions at (a) 850 and (b) 1000 °C using KAM1-GS gas phase kinetics feeding the gas composition experimentally obtained from the outlet of first reactor.
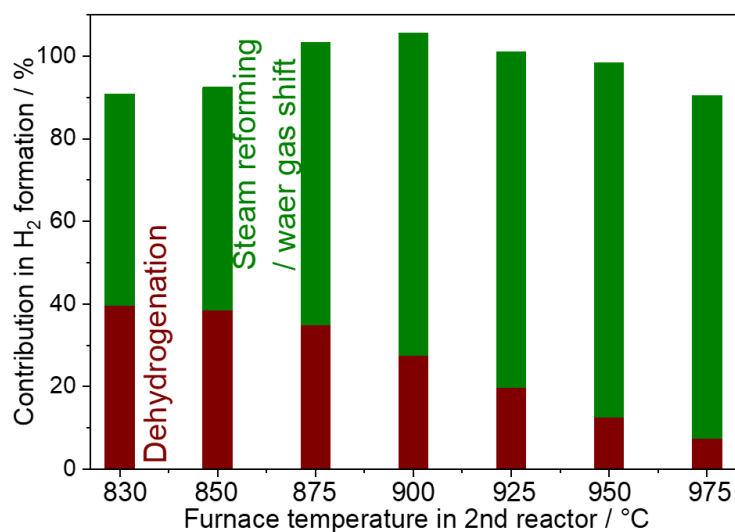
Figure S4. Contributions in H_2 formation estimated from C_2H_6 consumption and CO_x formation in the second reactor filled with 800 mg of catalysts (5 wt% Na_2WO_4/SiO_2) at 830 - 975 °C. The first reactor; 800 mg of 5 wt% Na_2WO_4/SiO_2 at 850 °C. Inlet gas; CH_4 10 kPa, O_2 1.4 kPa, H_2O 1.7 kPa, total pressure 101 kPa, Ar balance, 40 mL min^{-1}. O_2 is depleted in all the conditions. Corresponding data is shown in Fig. 6b.

Supplementary note 1: Contribution in H_2 formation in the second reactor filled with catalysts

In the second reactor filled with 800 mg of catalysts (5 wt% Na_2WO_4/SiO_2), we have compared 1) total H_2 formed, 2) estimated H_2 formed by dehydrogenation of C_2H_6 to C_2H_4, and 3) estimated H_2 formed by steam reforming / water gas shift reactions to CO_x.
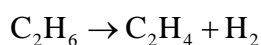
1)   Total H_2 formed, $\varDelta H_2$
$\varDelta H_2$ was obtained from the H_2 concentration measured at the outlet of first and second reactor.

$$\Delta H_2 = H_2(\text{2nd outlet}) - H_2(\text{1st outlet})$$

2)   Estimated H_2 formed by dehydrogenation of C_2H_6 to C_2H_4, $\varDelta H_2(C_2H_6$ consumption)
We assume the consumption of C_2H_6 in the second reactor fully comes from the following equation.

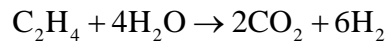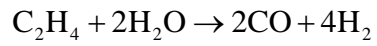$$C_2H_6 \rightarrow C_2H_4 + H_2$$

$\varDelta H_2(C_2H_6$ consumption) was estimated from the measured C_2H_6 concentration at the outlet of first and second reactor.

$$\Delta H_2(C_2H_6 \text{ consumption}) = C_2H_6(\text{1st outlet}) - C_2H_6(\text{2nd outlet})$$

3)   Estimated H_2 formed by steam reforming and water gas shift reactions to CO_x, $\varDelta H_2(CO_x$ formation)
We assume the formation of CO_x in the second reactor fully comes from the reaction with H_2O in the following equations according to oxygen balance.

$$C_2H_4 + 2H_2O \rightarrow 2CO + 4H_2$$

$$C_2H_4 + 4H_2O \rightarrow 2CO_2 + 6H_2$$

$\mathit{\Delta}H_2(CO_x$ formation) was estimated from the measured CO_x concentration at the outlet of first and second reactor.

$$\Delta H_2(CO_x \text{ formation}) = 2 \times \big(CO(\text{2nd outlet}) - CO(\text{1st outlet})\big) + 3 \times \big(CO_2(\text{2nd outlet}) - CO_2(\text{1st outlet})\big)$$

Their contributions are compared following the equations below and shown in Fig. S4.

$$H_2(\text{Dehydrogenation}) = \Delta H_2(C_2H_6 \text{ consumption})/\Delta H_2 \times 100$$

$$H_2(\text{Steam reforming / water gas shift}) = \Delta H_2(CO_x \text{ formation})/\Delta H_2 \times 100$$

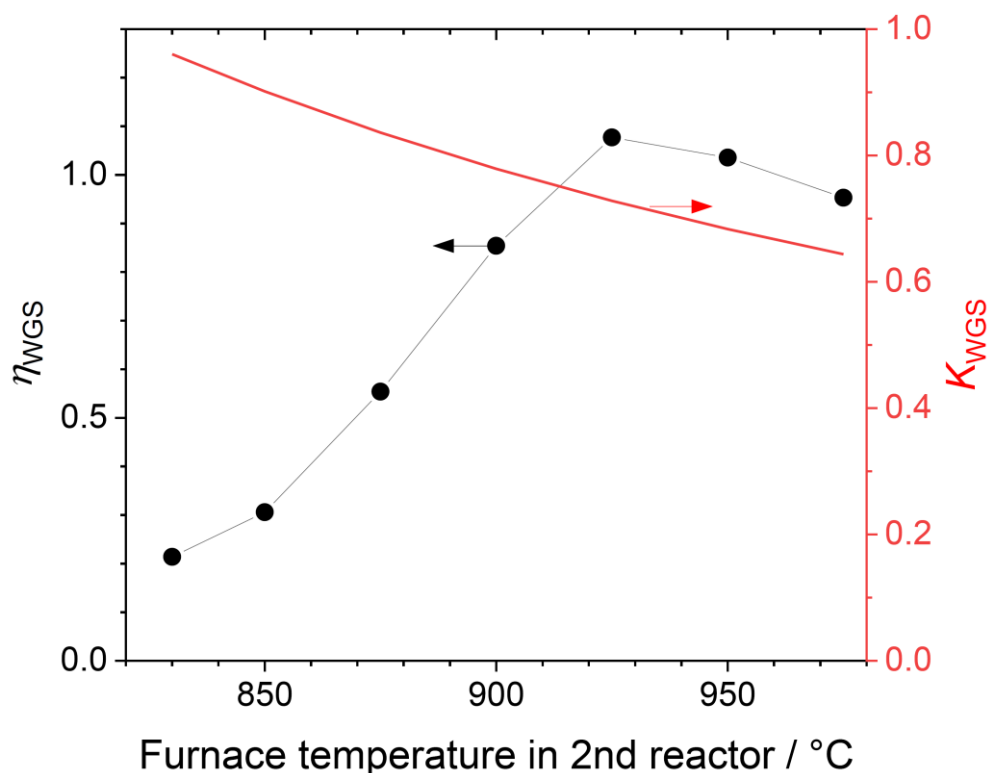**Figure S5.** The equilibrium constant of water gas shift reaction, K_{WGS},[1] and η_{WGS} ($\eta_{WGS} = P_{CO_2} P_{H_2} / P_{CO} P_{H_2O} K_{WGS}$) estimated from the partial pressures in the outlet from the second reactor filled with 800 mg of catalysts (5 wt% Na_2WO_4/SiO_2) at 830 - 975 °C. The first reactor was filled with 800 mg of 5 wt% Na_2WO_4/SiO_2 at 850 °C. The partial pressure of H_2O was estimated from the oxygen balance using the concentrations of the introduced O_2 and H_2O in the inlet and the measured CO and CO_2 in the outlet. Inlet gas; CH_4 10 kPa, O_2 1.4 kPa, H_2O 1.7 kPa, total pressure 101 kPa, Ar balance, 40 mL min^{-1}.

Reference

1 CA. Callaghan, *Kinetics and catalysis of the water-gas shift reaction: a microkinetic and graph theoretic approach*. PhD Thesis, Department of Chemical Engineering, Worcester Polytechnic Institute, Worcester, MA, 2006