

Supporting Information

An Approach Using Oxidative Coupling of Methane for Converting Biogas and Acid Natural Gas into High-Calorific Fuels

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Catalyst preparation

La_2O_3 and MgO were used as host oxides. An incipient wetness impregnation method was applied for depositing an aqueous solution of two dopants to each host oxide at room temperature. The dopants were nitrates of lithium, cesium, barium, strontium, manganese or magnesium (in case of La_2O_3 as host oxide). The impregnated materials were dried at 120 °C for 4 hours followed by their calcination in a muffle furnace in static air at 800 °C for 5 hours. Hereafter, they were pressed and then crushed to obtain particles of 0.25 - 0.45 mm.

Higher heating value calculations

For calculating higher heating value (HHV) of gaseous mixtures formed in the OCM reaction over different catalysts from the database reported by Kondratenko et al.[E.V. Kondratenko, T. Peppel, D. Seeburg, V.A. Kondratenko, N. Kalevaru, A. Martin, S. Wohlrab, Catal. Sci. Tech. 7 (2017) 366-381], the below assumptions were made:

- i. water and oxygen are not present in the mixtures;
- ii. C_2H_4 and C_2H_6 are present in equal amounts or outlet mixtures contains either C_2H_4 or C_2H_6 (unfortunately, separate selectivity values for C_2H_4 and C_2H_6 are often not reported);
- iii. CO_2 and CO are present in equal amounts or outlet mixtures contains either CO_2 or CO (unfortunately, separate selectivity values for CO_2 and CO are often not reported).

On the basis of (ii) and (iii), we calculated averaged higher heating values for C_2 hydrocarbons and CO_x using equations S1 and S2 respectively. Equation S3 was used to calculate overall HHV.

$$HHV_{C_2} = (HHV_{C_2H_6} + HHV_{C_2H_4})/2 \quad (S1)$$

$$HHV_{CO_x} = (HHV_{CO_2} + HHV_{CO})/2 \quad (S2)$$

$$HHV = \chi_{CH_4} \times HHV_{CH_4} + \chi_{C_2} \times HHV_{C_2} + \chi_{CO_x} \times HHV_{CO_x} \quad (S3)$$

Where χ_{CH_4} , χ_{C_2} , χ_{CO_x} are mole fractions of CH_4 , C_2 hydrocarbons and CO_x respectively.

$$HHV_{C_2H_6} = 19.682 \text{ kW} \cdot \text{h} \cdot \text{m}^{-3}$$

$$HHV_{C_2H_4} = 17.756 \text{ kW} \cdot \text{h} \cdot \text{m}^{-3}$$

$$HHV_{CO_2} = 0 \text{ kW} \cdot \text{h} \cdot \text{m}^{-3}$$

$$HHV_{CO} = 3.537 \text{ kW} \cdot \text{h} \cdot \text{m}^{-3}$$

As previous studies did not report mole fractions of individual components as required for calculating HHV (equation S3), we calculated them from the reported values of C_2 and CO_x selectivity as well as CH_4 conversion as follows.

$$n_{CH_4} = n^0 \times (1 - X_{CH_4}) \quad (S4)$$

$$n_{C_2} = 0.5 \times n^0 \times S_{C_2} \times X_{CH_4} \quad (S5)$$

$$n_{CO_x} = n^0 \times S_{CO_x} \times X_{CH_4} = n^0 \times X_{CH_4} \times (1 - S_{C_2}) \quad (S6)$$

$$\chi_{CH_4} = \frac{n^0 \times (1 - X_{CH_4})}{n^0 \times (1 - X_{CH_4}) + 0.5 \times n^0 \times X_{CH_4} \times S_{C_2} + n^0 \times X_{CH_4} \times (1 - S_{C_2})} = \frac{1 - X_{CH_4}}{(1 - 0.5 \times X_{CH_4} \times S_{C_2})} \quad (S7)$$

$$\chi_{C_2} = \frac{0.5 \times n^0 \times X_{CH_4}}{n^0 \times (1 - X_{CH_4}) + 0.5 \times n^0 \times X_{CH_4} \times S_{C_2} + n^0 \times X_{CH_4} \times (1 - S_{C_2})} = \frac{0.5 \times X_{CH_4} \times S_{C_2}}{(1 - 0.5 \times X_{CH_4} \times S_{C_2})} \quad (S8)$$

$$\chi_{CO_x} = \frac{n^0 \times X_{CH_4} \times (1 - S_{C_2})}{n^0 \times (1 - X_{CH_4}) + 0.5 \times n^0 \times X_{CH_4} \times S_{C_2} + n^0 \times X_{CH_4} \times (1 - S_{C_2})} = \frac{X_{CH_4} \times (1 - S_{C_2})}{(1 - 0.5 \times X_{CH_4} \times S_{C_2})} \quad (S9)$$

Using equations S3-S9, equation S10 can be obtained. It shows the dependence of C_2 selectivity on CH_4 conversion to get a gas mixture with a certain HHV.

$$S_{C_2} = \frac{HHV - (1 - X_{CH_4}) \times HHV_{CH_4} - X_{CH_4} \times HHV_{CO_x}}{0.5 \times HHV \times X_{CH_4} + 0.5 \times X_{CH_4} \times HHV_{C_2} - X_{CH_4} \times HHV_{CO_x}} \quad (S10)$$

Where, n_i , n^0 , X_{CH_4} , S_{C_2} , S_{CO_x} stand for the number of moles of an individual component (CH_4 , C_2 hydrocarbons or CO_x), the number of methane moles in the feed mixture, methane conversion, C_2 selectivity and CO_x selectivity respectively.

If CO_2 is present in the OCM feed, equation S10 is transformed to equation S11.

$$S_{C_2} = \frac{HHV(1+a) - (1 - X_{CH_4}) \times HHV_{CH_4} - X_{CH_4} \times HHV_{CO_x}}{0.5 \times HHV \times X_{CH_4} + 0.5 \times X_{CH_4} \times HHV_{C_2} - X_{CH_4} \times HHV_{CO_x}} \quad (S11)$$

Where a is the feed ratio of CO_2 to CH_4 .

Table S1 Catalyst composition and their performance in the OCM reaction at 800°C using a feed (40 vol% CH₄) with the CH₄/O₂ ratio of 2.

| Nr. | Catalysts | X(CH ₄) / % | Y(C ₂) / % | S(C ₂) / % | S(C ₃₊) / % | S(CO _x) / % | C ₂ H ₆ / C ₂ H ₄ | CO/ CO ₂ |
|-----|---|----------------------------|---------------------------|---------------------------|----------------------------|----------------------------|--|------------------------|
| 1 | Mn _{0.1} Sr _{9.1} La _{90.8} O _x | 22.8 | 8.6 | 37.5 | n.m. | 60.5 | 0.75 | 0.12 |
| 2 | Li _{0.1} Sr _{9.1} La _{90.8} O _x | 25.5 | 11.3 | 44.5 | n.m. | 55.5 | 0.64 | 0.12 |
| 3 | Mn _{0.1} Ba _{1.0} La _{98.9} O _x | 34.5 | 11.8 | 34.2 | n.m. | 65.8 | 0.93 | 0.09 |
| 4 | Mg _{8.3} Sr _{8.3} La _{83.3} O _x | 38.5 | 14.8 | 38.4 | n.m. | 61.6 | 0.64 | 0.15 |
| 5 | Mg _{9.1} Ba _{0.9} La _{90.1} O _x | 39.5 | 16.6 | 42.0 | n.m. | 58.0 | 0.66 | 0.15 |
| 6 | Ba _{8.3} Sr _{8.3} Mg _{83.3} O _x | 39.8 | 17.4 | 43.7 | n.m. | 56.3 | 0.58 | 0.13 |
| 7 | Cs _{8.3} Sr _{8.3} Mg _{83.3} O _x | 40.6 | 17.6 | 43.3 | n.m. | 56.7 | 0.57 | 0.21 |
| 8 | Mn-Na-WO _x /SiO ₂ | 48.0 | 20.2 | 42.0 | 3.4 | 54.6 | 0.3 | 0.04 |

n.m. stands for not measured.

$$Y(C_2)=X(CH_4)*S(C_2)/100 \quad (12)$$

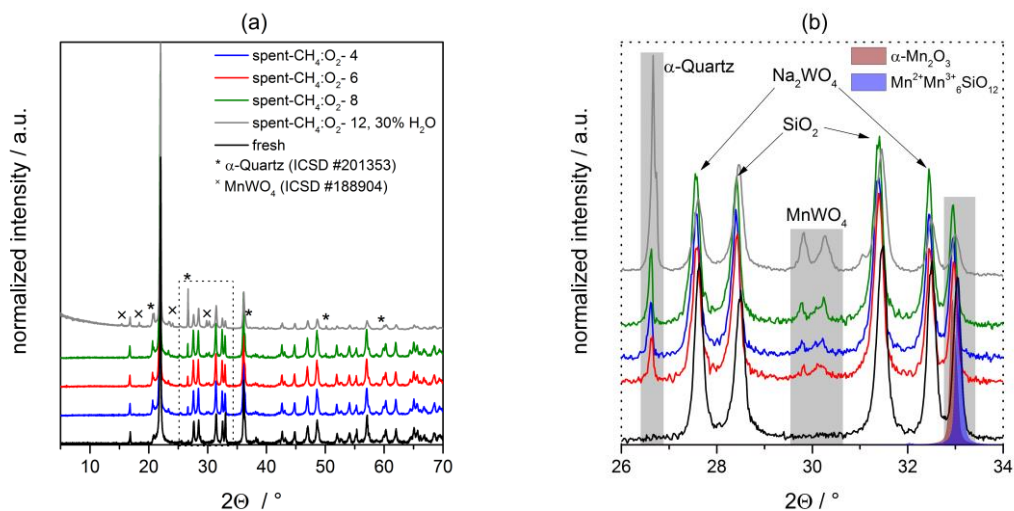


Figure S1 (a) X-ray diffractograms of fresh and spent (after the OCM reaction at 800°C using feeds with different CH_4/O_2 ratios) Mn-Na- WO_x/SiO_2 and (b) magnification of the dashed box from (a) to identify structural changes after OCM reaction.

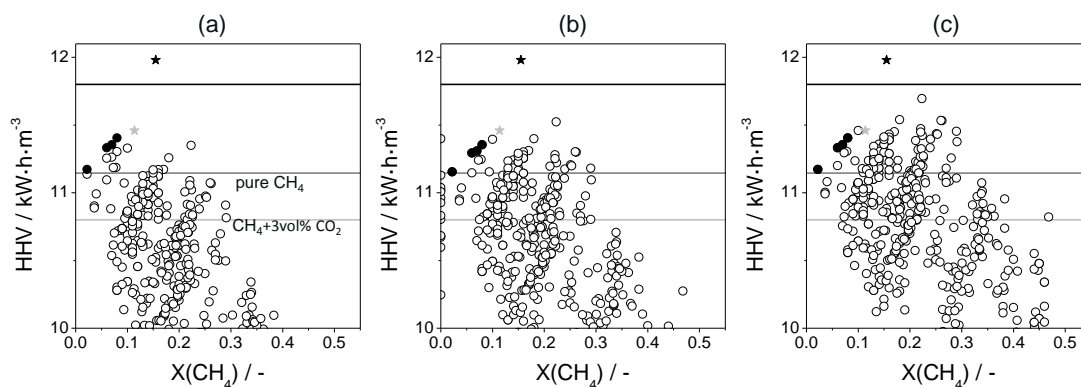


Figure S2 Higher heating value (HHV) of gas mixtures after the OCM reaction over different catalysts from the database reported by Kondratenko et al.[E.V. Kondratenko, T. Peppel, D. Seeburg, V.A. Kondratenko, N. Kalevaru, A. Martin, S. Wohlrab, Catal. Sci. Tech. 7 (2017) 366-381]. As separate selectivity values for CO₂, CO, C₂H₆ and C₂H₄ have not always been reported in the previous studies it was assumed for calculations that (a) the outlet mixture consists of CH₄, C₂H₄ and CO₂, (b) the outlet mixture consists of CH₄, C₂H₄/C₂H₆=1 and CO/CO₂=1, (c) the outlet mixture consists of CH₄, C₂H₆ and CO. The stars represent the performance after OCM (grey symbol) and after OCM combined with hydrogenation of carbon oxides (black symbol) as obtained in this study. The solid lines in this figure represent HHV of 10.7, 11.147, and 11.8 kW·h·m⁻³ characteristic of biogas with 3 vol% CO₂, pure CH₄ and the high calorific natural gas[Terry, W.; Nigel, B.; Martin, B.; Len, E.; Adam, J.; Antony, K.; Angus, P.; Gareth, D.; Andrew, M.; James, C.; James, W.; Michael, d. C.; Seda, F.; Natasha, A.; Sergej, D. Final Report, Gas Quality Harmonisation Cost Benefit Analysis; The European Commission by GL Noble Denton and Pöyry Management Consulting, 2012.], respectively.

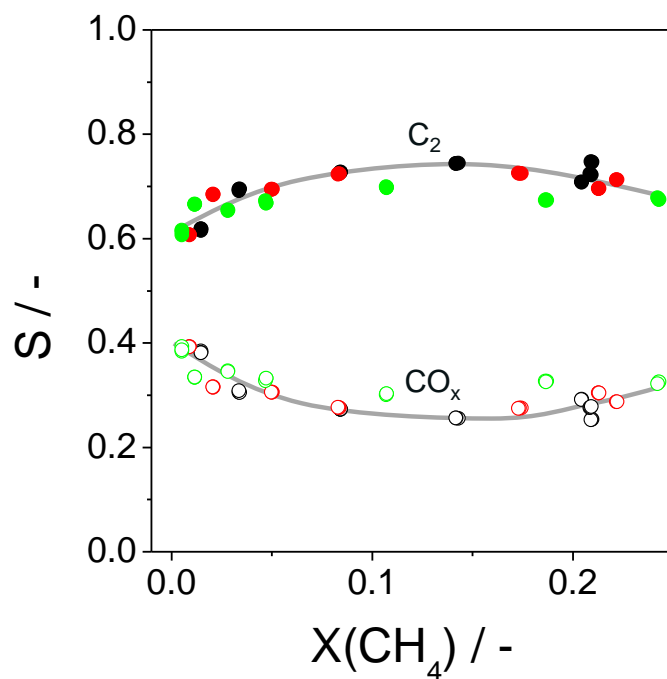


Figure S3 Effect of methane conversion on the selectivity (S) to C_2 hydrocarbons (closed symbols) and CO_x (open symbols) over $\text{Mn-Na-WO}_x/\text{SiO}_2$ at 800°C using reaction feeds with 20 (green), 40 (red) or 70 (black) vol% CH_4 . The CH_4/O_2 ratio was 6.

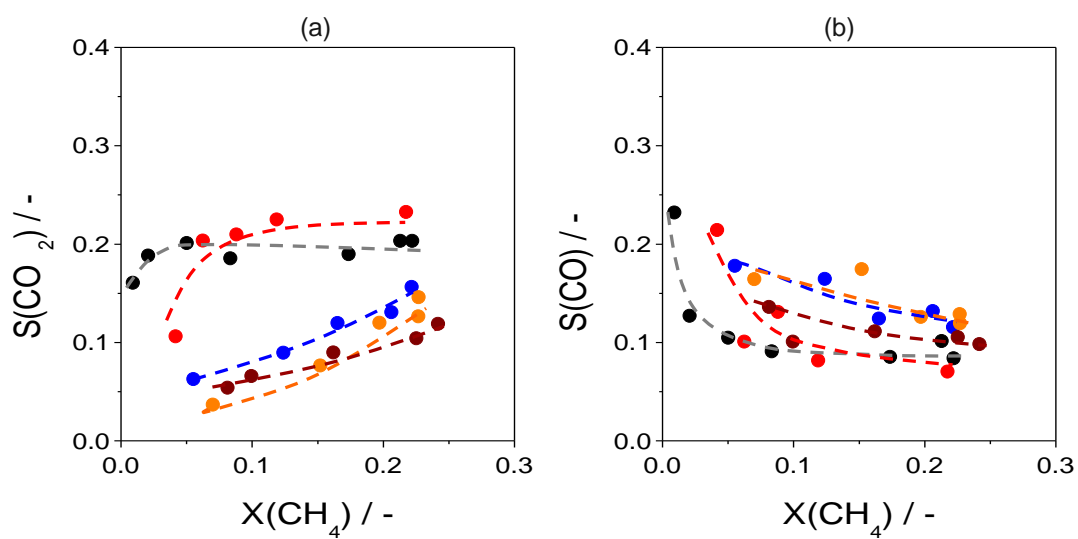


Figure S4 Effect of methane conversion on the selectivity to (a) CO_2 and (b) CO over $\text{Mn-Na-WO}_x/\text{SiO}_2$ at 800°C using a feed (40 vol% CH_4) with the CH_4/O_2 ratio of 6 and different amounts of co-fed water: ● 0, ● 2, ● 5, ● 15, ● 30 vol%.