

Supplementary Information

Oxidative Coupling of Methane for Ethylene Production: Reviewing Kinetic Modelling Approaches, Thermodynamics and Catalysts

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Contents

Section S1.....	2
Table S1.....	3
Figure S1.....	4
Figure S2.....	5
Figure S3.....	6

Section S1 – Yields and Selectivities definitions

The yield of the compound i (Y_i) was calculated in carbon base, using Eq. (A1), where n_i is the number of mols of the component i at the equilibrium, c_i is the number of carbon atoms of the compound i , and n_{0,CH_4} denotes the initial number of mols of methane.

$$Y_i (\%) = \frac{(c_i \cdot n_i) \cdot 100}{(n_{0,CH_4})} \quad (A1)$$

The C2 thermodynamic yield represents the combined yield from ethene and ethane, as defined in Eq. (A2).

$$Y_{C_2} (\%) = \frac{(2 \cdot n_{C_2H_4} + 2 \cdot n_{C_2H_6}) \cdot 100}{(n_{0,CH_4})} \quad (A2)$$

Selectivities were calculated in carbon base, according to Eq. (A3), where NC_c is the number of reaction products containing carbon.

$$S_i (\%) = \frac{c_i \cdot n_i \cdot 100}{\sum_{i=1}^{NC_c} (c_i \cdot n_i)} \quad (A3)$$

Selectivities in molar base were defined as Eq. (A4), where NC is the number of reaction products.

$$S_i (\%) = \frac{n_i \cdot 100}{\sum_{i=1}^{NC} n_i} \quad (A4)$$

Carbon based ethene yield in the presence of ethane co-feeding was calculated as Eq. (A5), where n_{0,C_2H_6} denotes the initial number of mols of ethane.

$$Y_{C_2H_4} (\%) = \frac{(2 \cdot n_{C_2H_4}) \cdot 100}{(n_{0,CH_4} + 2 \cdot n_{0,C_2H_6})} \quad (A5)$$

Table S1 - Standard Gibbs energies in increasing order at 900 °C and standard reaction enthalpies for global OCM reactions [1,2].

Entry	Reaction	ΔG° at 900 °C (kJ·mol ⁻¹)	ΔH_{298° (kJ·mol ⁻¹)
1	$C_2H_4 + 2O_2 \rightarrow 2CO + 2H_2O$	-928	-757
2	$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	-798	-802
3	$CH_4 + \frac{3}{2}O_2 \rightarrow CO + 2H_2O$	-618	-519
4	$CH_4 + O_2 \rightarrow CO + H_2O + H_2$	-436	-278
5	$CO + \frac{1}{2}O_2 \rightarrow CO_2$	-180	-283
6	$C_2H_4 + 2H_2O \rightarrow 2CO + 4H_2$	-198	210
7	$C_2H_6 + \frac{1}{2}O_2 \rightarrow C_2H_4 + H_2O$	-197	-105
8	$2CH_4 + \frac{1}{2}O_2 \rightarrow C_2H_6 + H_2O$	-112	-177
9	$C_2H_6 \rightarrow C_2H_4 + H_2$	-14.73	137
10	$CO_2 + H_2 \rightarrow CO + H_2O$	-1.78	41
11	$CO + H_2O \rightarrow CO_2 + H_2$	1.78	-41

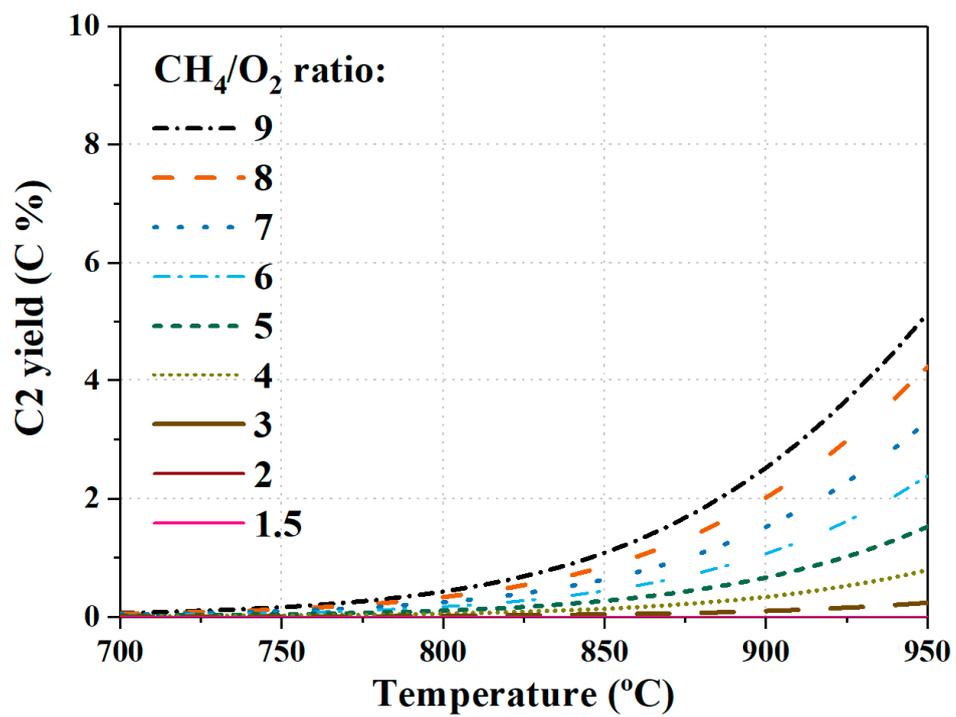


Figure S1 - Effect of the CH₄/O₂ feed ratio and temperature at 1 bar on the combined ethene and ethane (C₂) yield. Feed composition was constituted by CH₄ and O₂ only and was varied while keeping the total number of mols fed fixed.

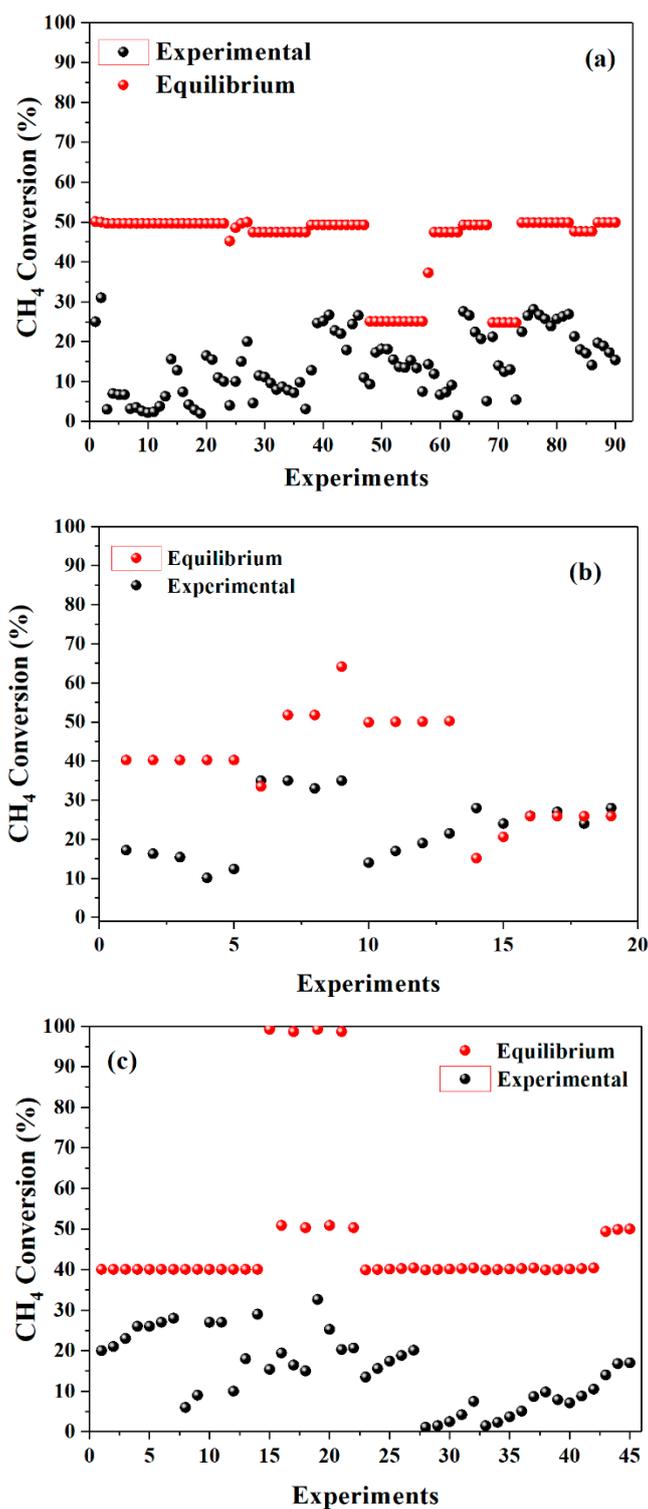


Figure S2 - Comparison between experimental and equilibrium CH₄ conversions for bimetallic oxides: (a) promoted or supported alkaline earth metals oxides, (b) involving lanthanoids metals oxides, and (c) transition or post-transition metals oxides. Equilibrium calculations were performed using the Gibbs minimisation method, as described in Section 4.

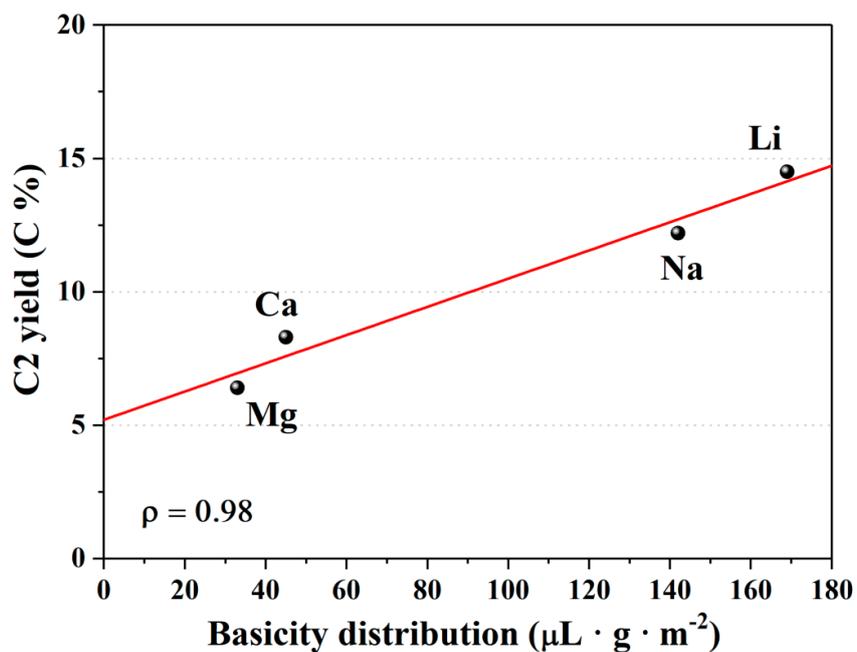


Figure S3 – Relationship between C2 yield and basicity distribution per unit of surface area, as calculated from the ratio between the volume of desorbed CO₂, in μL, and the surface area, in m²·g⁻¹, over M-TbO_x/n-MgO systems. The alkali or alkaline earth metal *M* is indicated in the figure. Catalytic activity was assessed at 700 °C, with CH₄/O₂ feed molar ratio of 4, after 15 min of reaction time [3].

References

- [1] Valadkhani, A.; Shahrokhi, M.; Pishvaie, M. R.; Zarrinpashneh, S. Simulation and Experimental Studies of Methane Oxidative Coupling Reaction in a Bench Scale Fixed Bed Reactor. *Energy Sources, Part A Recover. Util. Environ. Eff.* **2013**, *35* (15), 1418–1426. <https://doi.org/10.1080/15567036.2010.520070>.
- [2] Stansch, Z.; Mleczko M, L.; Baerns. Comprehensive Kinetics of Oxidative Coupling of Methane over the La₂O₃/CaO Catalyst. *Ind. Eng. Chem. Res.* **1997**, *36* (7), 2568–2579. <https://doi.org/10.1021/ie960562k>.
- [3] Elkins, T. W.; Roberts, S. J.; Hagelin-Weaver, H. E. Effects of Alkali and Alkaline-Earth Metal Dopants on Magnesium Oxide Supported Rare-Earth Oxide Catalysts in the Oxidative Coupling of Methane. *Appl. Catal. A Gen.* **2016**, *528*, 175–190. <https://doi.org/10.1016/j.apcata.2016.09.011>.