

Electronic Supplementary Information

Oxidative coupling of methane over sodium zirconate catalyst

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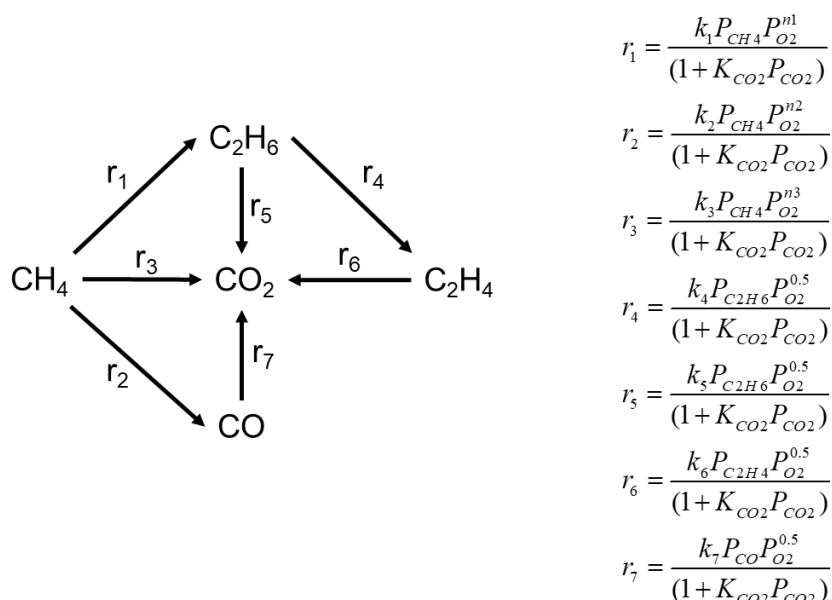
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Simplified kinetic model and parameter fitting

The kinetic model and rate equations are shown in Scheme S1. As it was demonstrated that the addition of CO₂ decreased the CH₄ consumption rate, we assumed that CO₂ competes with hydrocarbon species for active sites, thus the CO₂ adsorption term was included in all steps. In some simplified reaction networks, CO and CO₂ are lumped into one pseudocomponent CO_x, but for a more accurate description of O₂ consumption, it was necessary to explicitly treat the oxidation of CO to CO₂, especially in the case of Na₂ZrO₃ which has a known activity for CO oxidation. The O₂ reaction orders of the primary reactions (r₁, r₂, and r₃) were considered as independent parameters, but to limit the degree of freedom in the model, the rates of secondary reactions (r₄, r₅, r₆, and r₇) were assumed to follow the kinetics of dissociatively adsorbed O₂ (i.e. to vary with O₂ to 0.5 order). To allow for fitting to experimental data from different temperatures, each rate constant was assumed to have an Arrhenius-type temperature dependence ($k = A \exp(-E_a/RT)$, where A is the pre-exponential factor and E_a is the apparent activation energy). The adsorption equilibrium constant of CO₂ (K_{CO₂}) was also considered to vary with temperature: $K = K_{\infty} \exp(-\Delta H/RT)$, where K_∞ is the equilibrium constant in the high-temperature limit and ΔH is the enthalpy of CO₂ adsorption, assumed to be constant over the experimental temperature range of 700 – 800 °C.

In preliminary model fitting, the adsorption term for CH₄ was also included, but the obtained value was close to zero, indicating that it was negligible. As the experimental selectivity of C₂H₂ was <0.2 % in all runs, C₂H₂ was not included in the kinetic modelling. C₃ and C₄ species were <3 %, and these were bundled with C₂H₄ selectivity for modelling purposes. Additional reaction pathways were also considered (the nonoxidative dehydrogenation of C₂H₆, the oxidation of C₂H₆ and C₂H₄ to CO, the backwards reaction of CO₂ to CO) but their contributions were negligible under the selected conditions.

Figure S1 demonstrates the fit at 750 °C between the model and the experimental product distributions, CH₄ conversion, and C₂ yield, under various contact times (defined as the weight of the catalyst divided by the total flow rate, with the



Scheme S1. Simplified reaction scheme and rate equations for OCM.

dimensions of g_{cat} s mL⁻¹). These results show that the simplified reaction network, with 19 degrees of freedom (7 rate constants, 7 apparent activation energies, 3 O₂ reaction orders, the adsorption equilibrium constant of CO₂, and the enthalpy of adsorption of CO₂), fit well with the experimental dataset across a wide range of conditions. The average error of a product partial pressure was 12.1 % (calculated from averaging the percentage differences between experimental and calculated C₂H₆, C₂H₄, CO, and CO₂ pressures at each of the 150 datapoints).

The fitted parameters are shown in Table S1. The fitted O₂ reaction orders for the CO and CO₂ forming reactions were higher than 1, which is higher than that of the C₂H₆ forming reaction (r₁), indicating that the primary C₂ selectivity is strongly dependent on the concentration of O₂.

Table S1. Fitted kinetic parameters of Na₂ZrO₃. n is the total reaction order in the reaction steps 1-3. * denotes parameters that were kept constant.

Step number	O ₂ reaction order	Pre-exponential factor A (s ⁻¹ kPa ⁻ⁿ)	Apparent activation energy E _a (kJ mol ⁻¹)	rate constant k at 750 °C (s ⁻¹ kPa ⁻ⁿ)
1	0.31	9.10E+08	185	0.31
2	1.32	2.15E+00	32	0.053
3	1.48	4.30E+00	33	0.092
4	0.5*	1.07E+08	144	4.8
5	0.5*	2.23E+06	110	5.5
6	0.5*	2.40E+05	100	1.8
7	0.5*	2.64E+06	126	1.0

CO ₂ adsorption	High-temperature limit adsorption equilibrium constant K _∞ (kPa ⁻¹)	Enthalpy of adsorption ΔH (kJ mol ⁻¹)	adsorption equilibrium constant K at 750 °C (kPa ⁻¹)	
-	-	5.77E-11	-228	24

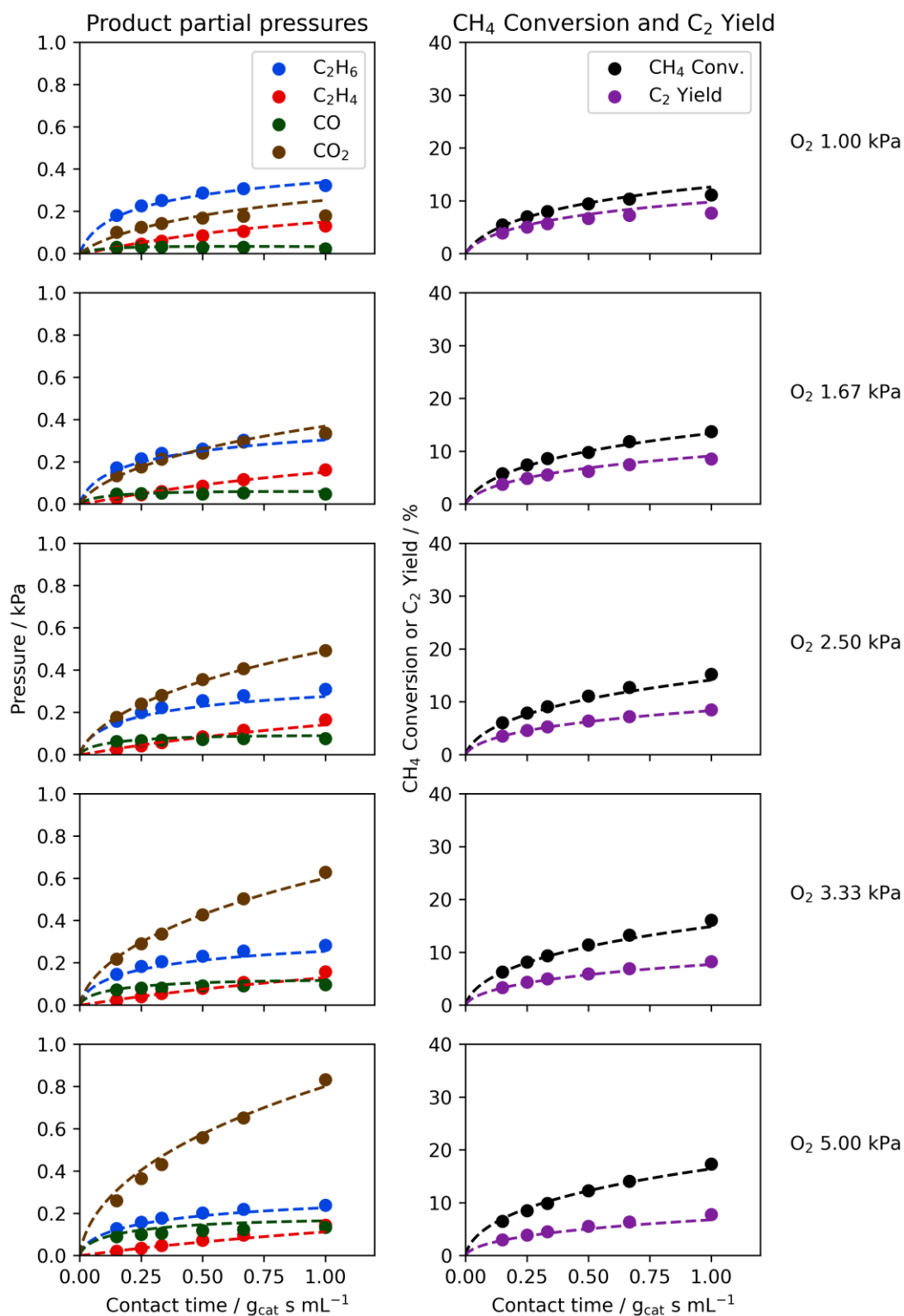


Figure S1. Experimental (points) and fitted model (dashed lines) product partial pressures, CH₄ conversion, and C₂ yield at various contact times. C₂H₆: blue, C₂H₄: red, CO: green, CO₂: brown, CH₄ conversion: black, C₂ yield: purple. Reaction conditions: catalyst 0.5 g, 750 °C, CH₄ 10 kPa, O₂ 1.0 – 5.0 kPa, total pressure 101 kPa (Ar balance), total flow rate 30 – 200 mL min⁻¹.

OCM performance of ZrO₂

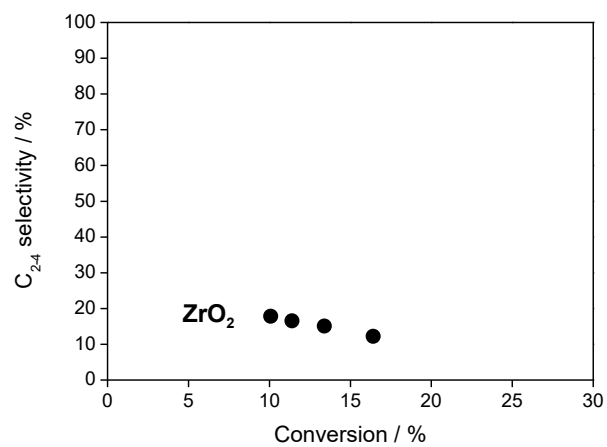


Figure S2. The OCM performance of ZrO₂. Reaction conditions: catalyst 0.2 g, 800 °C, CH₄ 10 kPa, O₂ 1.7 kPa, total pressure 101 kPa (Ar balance), total gas flow 30 - 150 mL min⁻¹.