Electronic Supplementary Information

Oxidative coupling of methane at elevated pressures:

Reactor concept and its validation

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$$X\ (CH_4 \text{ or } O_2) = 1 - \frac{\dot{n}^{outlet}_{CH_4 \text{ or } O_2}}{\dot{n}^{inlet}_{CH_4 \text{ or } O_2}} \cdot \frac{\dot{n}^{outlet}_{N_2}}{\dot{n}^{inlet}_{N_2}} \qquad \text{(eq.1)}$$

$$Y_i = 1 - \frac{a_i \cdot \dot{n}_i^{outlet}}{\dot{n}_{CH_4}^{inlet}} \cdot \frac{\dot{n}^{outlet}_{N_2}}{\dot{n}^{inlet}_{N_2}} < \qquad \text{(eq.2)}$$

$$S_i = \frac{Y_i}{X_{CH_4}} \qquad \text{(eq.3)}$$

X(i)	conversion of component *i*
$\dot{n}_i^{inlet}$	molar flow of component *i* at the reactor inlet
$\dot{n}_i^{outlet}$	molar flow of component *i* at the reactor outlet
Y_i	Yield of component *i*, relative to methane
a_i	number of carbon atoms in component *i*
S_i	Selectivity to component *i*, relative to methane

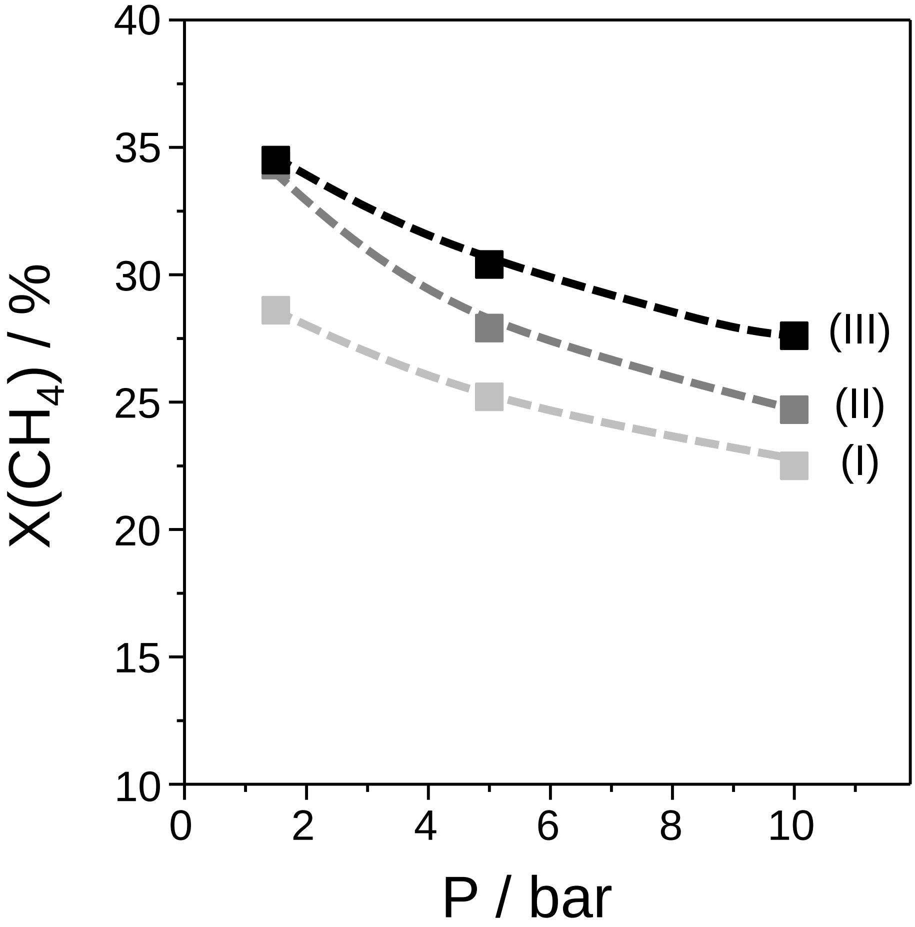

Figure S1 Methane conversion at 1123 K and different total pressures using a CH_4:O_2:N_2=4:1:15 feed. (I) reactor as described in Figure 1 and F_{total} = 50 ml/min, (II) reactor with reduced volume upstream to catalyst bed and F_{total} = 50 ml/min, (III): reactor with reduced volume upstream to catalyst bed and F = 100 ml/min (at 5 bar) or 400 ml/min (at 10 bar). Oxygen conversion was always complete.

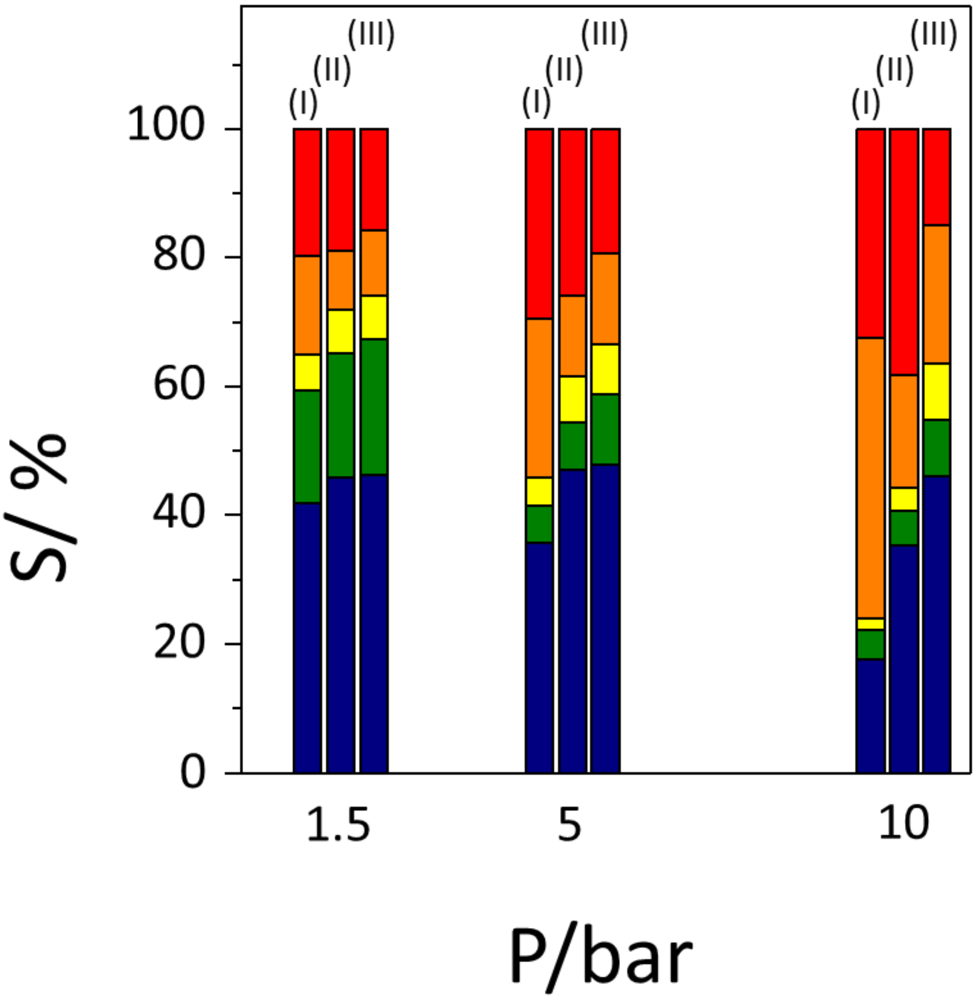

Figure S2 Product distribution of the OCM reaction at various pressures; (I): reactor as described in Figure 1, F = 50 ml/min, (II): reduced reactor volume, F = 50 ml/min, (III): reduced reactor volume, F = 100 ml/min (at 5 bar) or 400 ml/min (at 10 bar); 20 vol.% CH_4, CH_4:O_2 = 4:1, T = 1123 K, X (O_2) = 100 %; ●: C_2H_4, ●: C_2H_6, ●: C_{3+}, ●:CO, ●:CO_2

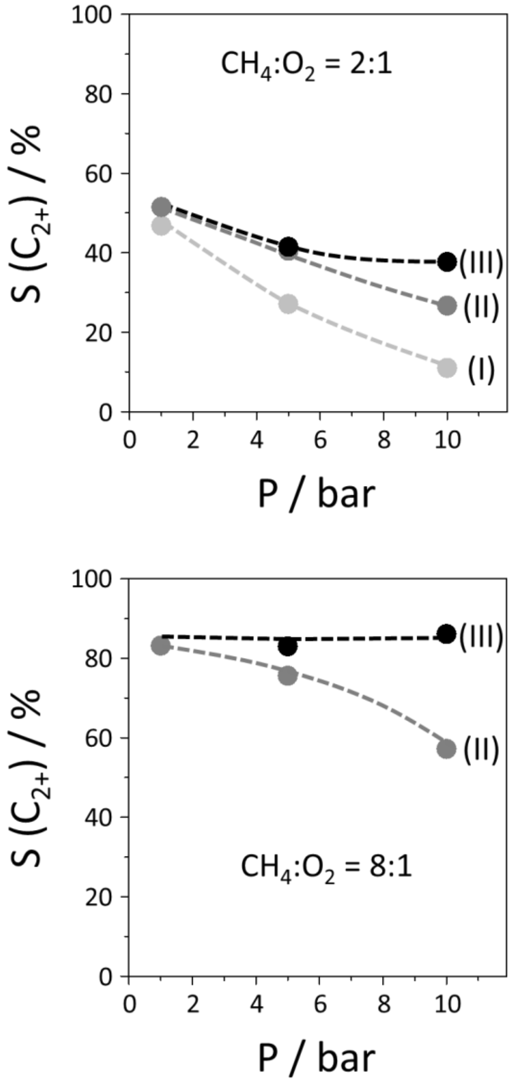

Figure S3 Selectivity to C_{2+} hydrocarbons in the OCM reaction at various pressures and reactant feeds; (I): reactor as described in Figure 1, F = 50 ml/min, (II): reduced reactor volume, F = 50 ml/min, (III): reduced reactor volume, F = 100 ml/min (at 5 bar) or 400 ml/min (at 10 bar); 20 vol.% CH_4, CH_4:O_2 = 4:1, T = 1123 K, X (O_2) = 100 %

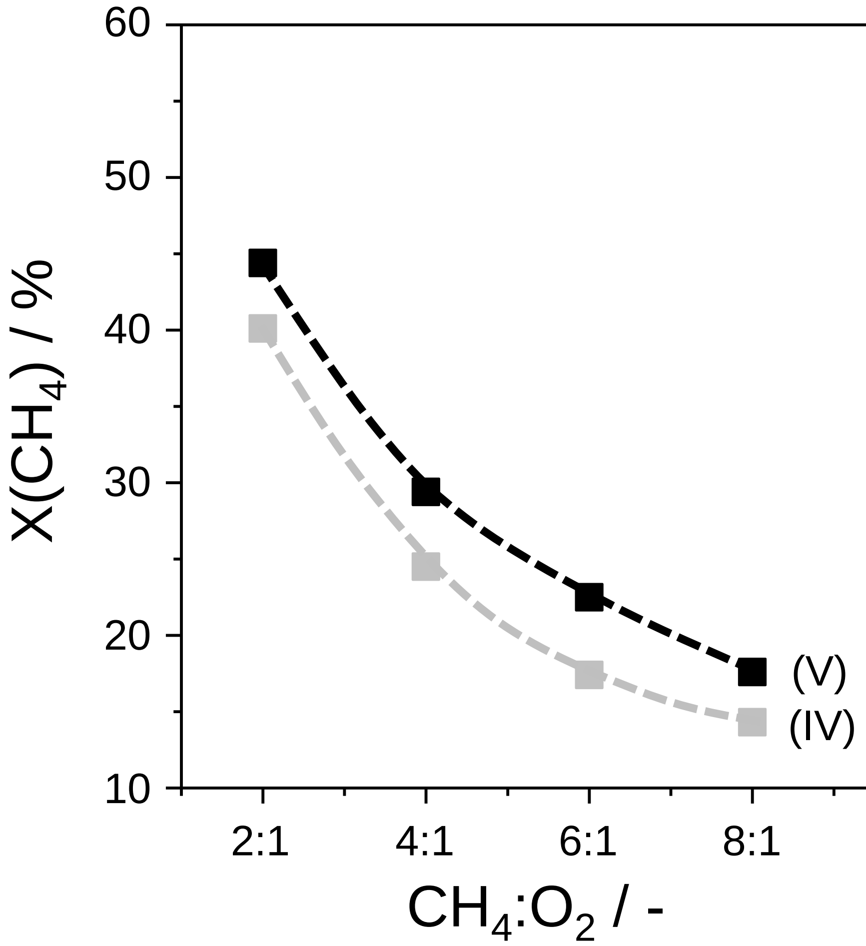

Figure S4 Effect of water and CH_4:O_2 ratio on CH_4 conversion at 1123 K and 10 bar.(IV) OCM feeds without water, (V) OCM feeds with 10 vol.% water (N_2 was partially replaced by H_2O). Further conditions: F_{total} = 100 ml/min, 20 vol.% CH_4, X (O_2) = 100 %. Reactor volume upstream to catalyst bed was reduced by installing a quartz glass rod.