**Supporting Information**

# Effect of Ethane and Ethylene on Catalytic Non Oxidative Coupling of Methane

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S.1 Product distribution as function of conversion level and product yield distribution when using the post-heater

SI Figure 1 and SI Figure 2 show the measured selectivity data as function of hydrocarbon conversion used for the interpolation of Figure 6 in the main text.
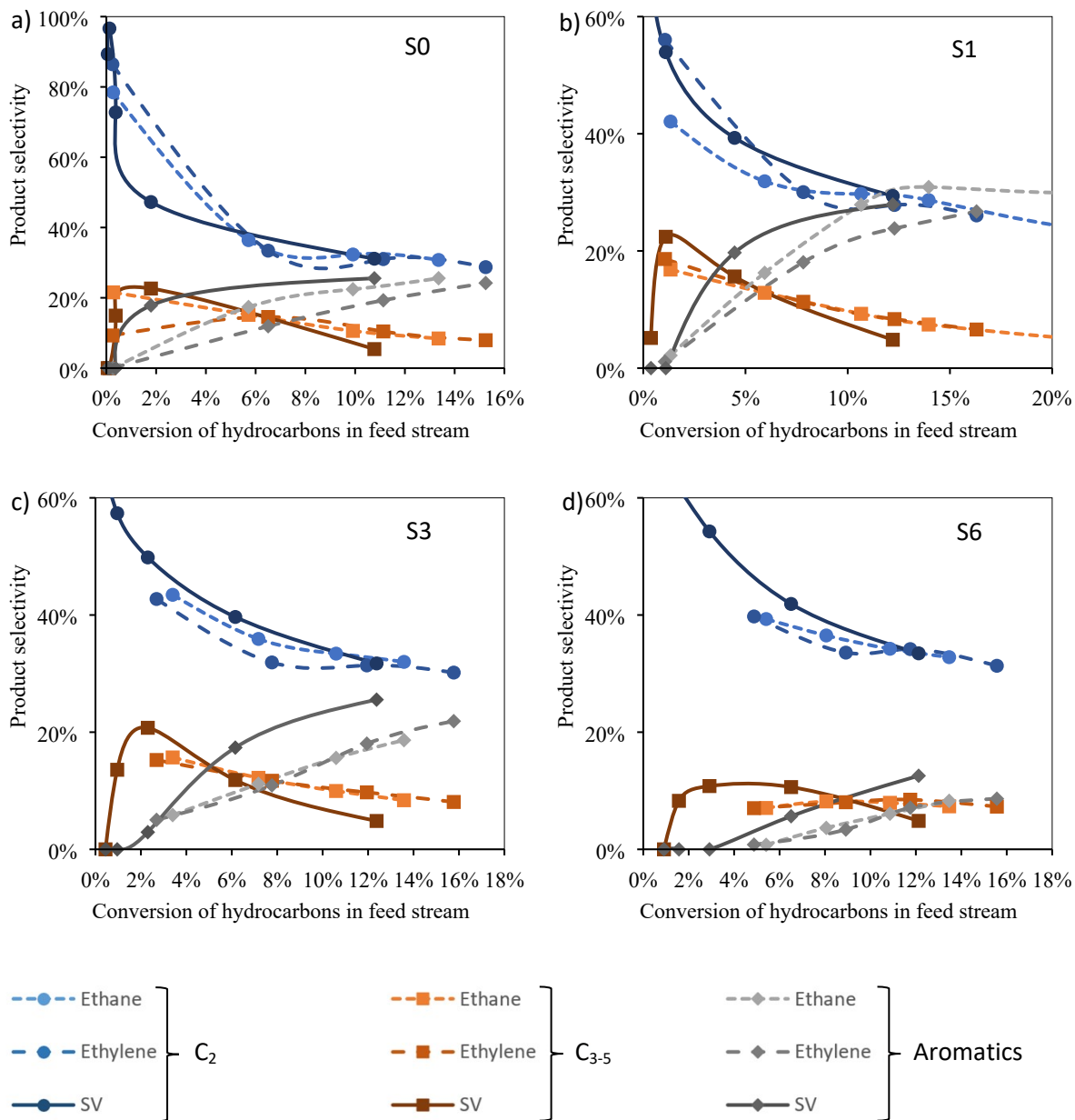

SI Figure 1: Selectivity distribution over major product groups as function of hydrocarbon conversion level, used to interpolate the data shown in Figure 6 in the main text and SI Figure 4, (a) a blank reactor, E0, (b) C1, (c) C3, (d) C6, 90% CH₄ N₂ balance; 16.6 ml/min total flowrate. Reactor-zone at 1000 °C, pre-heater and post-heater at 400 °C
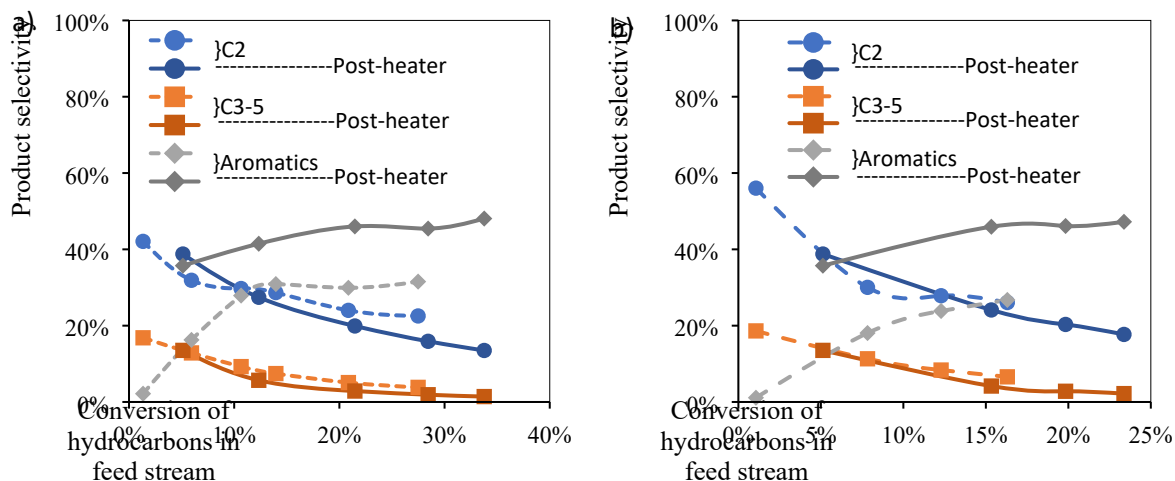
SI Figure 2: Selectivity distribution over major product groups as function of hydrocarbon conversion level for employing the post-heater compared to the C1 case without post-heater (shown in SI Figure 1), for (a) ethane and (b) ethylene addition used to interpolate the data shown in Figure 6 of the main text and supporting information SI Figure 4, , 90% CH$_4$ N$_2$ balance; 16.6 ml/min total flowrate. Reactor-zone at 1000 °C, pre-heater and post-heater at 1000 °C

Figure 3 shows the product yield distribution over all measured hydrocarbons when increasing the post-catalytic residence time by employing the post-heater. The same data presented in product groups is shown in Figure 7 in the main text.
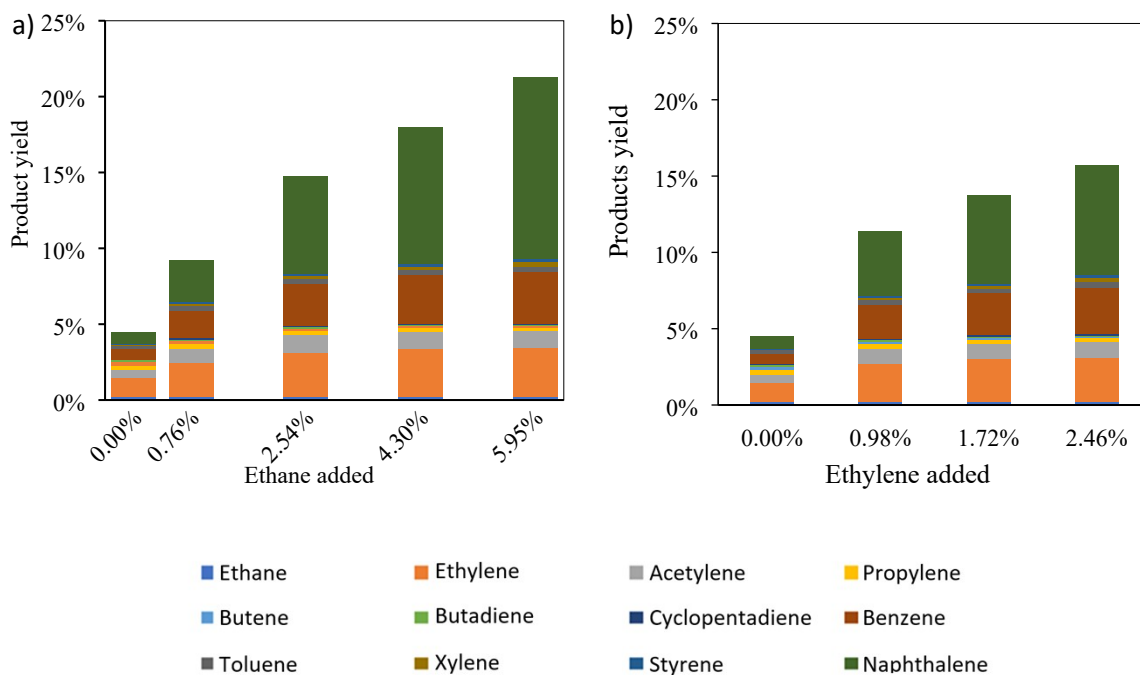

SI Figure 3: Product yield distribution as function of the volume of C$_2$ added to the reactant mixture for the C1 case including post-heater (a) ethane and (b) ethylene addition, 90% CH$_4$ N$_2$ balance; 16.6 ml/min total flowrate. Reactor-zone at 1000 °C, pre-heater and post-heater at 1000 °C

S.2   Product distribution per individual hydrocarbon at 10% total HC conversion

Figure 4 is a copy of Figure 6 in the main text, split out over all measured hydrocarbon products, rather than the grouped presentation in Figure 6. SI Figure 5 and SI Figure 6 show the same information as Figure 6 in the main text, but calculated in a different fashion. Figure 5 is interpolated at 10% methane conversion rather than the 10% conversion of fed-hydrocarbons in Figure 6. SI Figure 6 is calculated assuming partial conversion of the added C_2 compound, at 10% added hydrocarbon conversion.
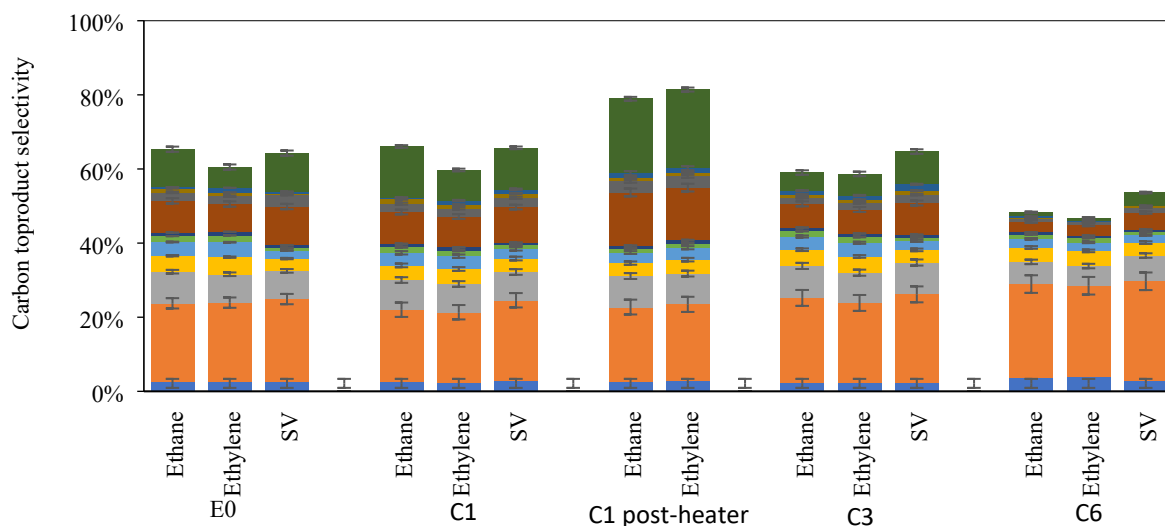
SI Figure 4: Product selectivity distribution for different methods of increasing methane conversion, by ethane addition or ethylene addition to the reactant mixture or by decreasing space velocity. The results have been linearly interpolated at 10% total hydrocarbon conversion as explained in the experimental section, Similarly selectivity is also calculated based on total hydrocarbon conversion. reactor-zone at 1000 °C; Pre-heater and post-heater are both at 400 °C, except for the C1 post-heater in that case $T_{postheater}$=1000 °C . The total flowrate for the cases with ethane or ethylene addition is 16.6 ml/min 90% CH_4, N_2 as balance. The graphs used for the interpolation can be found in supporting information SI Figure 1 and SI Figure 2.
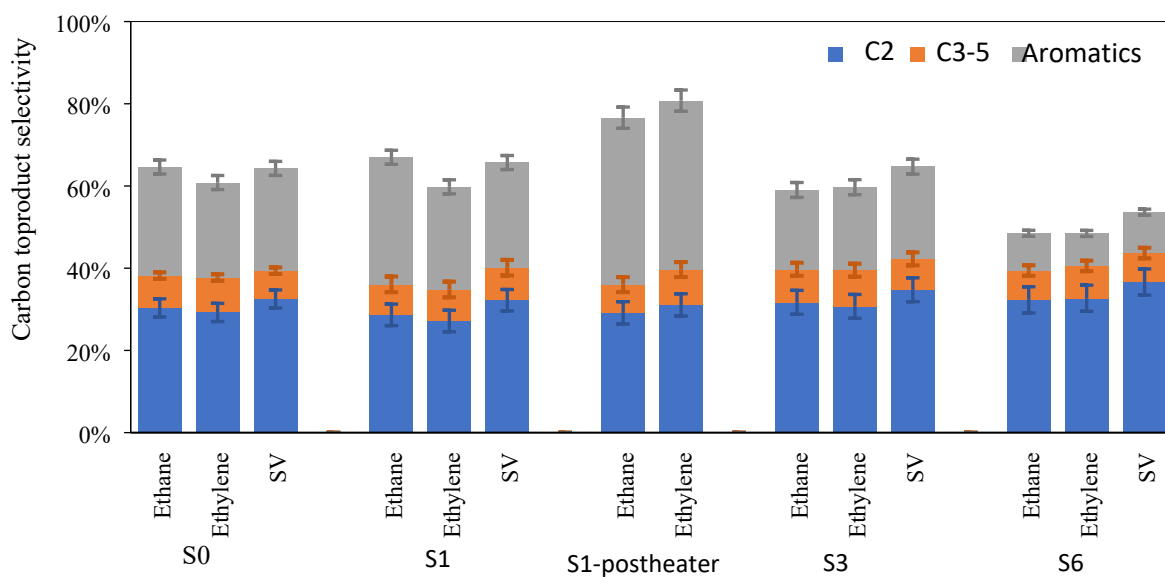
SI Figure 5: Product selectivity distribution for different methods of increasing methane conversion, by ethane addition or ethylene addition to the reactant mixture or by decreasing space velocity. The results have been linearly interpolated at 10% **CH₄ conversion**, *selectivity is calculated based on total conversion of hydrocarbons in the feed stream. reactor-zone at 1000 °C; Pre-heater and post-heater are both at 400 °C, except for the C1 post-heater in that case $T_{postheater}=1000 °C$. The total flowrate for the cases with ethane or ethylene addition is 16.6 ml/min 90% CH₄, N₂ as balance.*
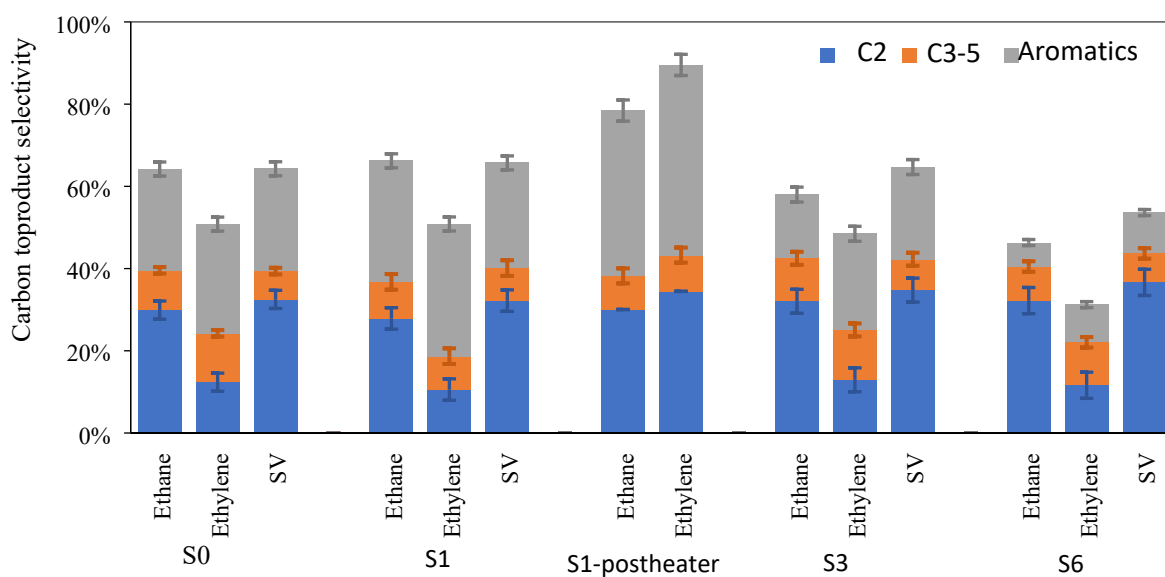
SI Figure 6: Product selectivity distribution for different methods of increasing methane conversion, by ethane addition or ethylene addition to the reactant mixture or by decreasing space velocity. The results have been linearly interpolated at 10% hydrocarbon conversion*, based on the partial conversion of methane (Figure 3 main text) and the partial conversion of the added C₂ molecule (main text Figure 4), selectivity is calculated based on hydrocarbon conversion discussed before. Note that this means that there is* **no** *ethane selectivity incase ethane is added and* **no** *ethylene selectivity when ethylene is added; the exception to this is the C1-post-heater case with ethane, since as main text Figure 4b shows, it has a* **negative** *ethylene conversion and thus a selectivity can be calculated. reactor-zone at 1000 °C; Pre-heater and post-heater are both at 400 °C, except for the C1 post-heater in that case $T_{postheater}=1000 °C$. The total flowrate for the cases with ethane or ethylene addition is 16.6 ml/min 90% CH₄, N₂ as balance.*

S.3   Deposit formation and mass balance analysis

SI Figure 7 shows the integral product yields of both coke-on-catalyst and deposits-downstream during a full experiment in which the concentration of added C_2 addition was varied between 0 and 2%. Coke-on-catalyst is measured with TGA and the formation of deposits-downstream of the catalyst is calculated based on the mass-balance. The experiment consists of the standard activation procedure as described in the experimental section and by Bao c.s. [1], followed by 2h of reaction using 90% CH_4 in N_2 without any addition of C_2. After that, the catalyst is exposed to three different C_2 concentrations (0.8-1.5-2.1 for C_2H_6 and 1.0-1.7-2.5 for C_2H_4) during 4 hours in total, keeping the total flowrate at 16.6 ml·min^{-1} and the methane concentration at 90%. Consequently, the catalyst is exposed to methane during 8h in total. There is no difference in coke-formation on the catalyst when adding either ethane or ethylene, shown in SI Figure 7a. Coke-on-catalyst formation increases more relative to the increase in catalyst mass added, showing the higher coking rates further downstream in the catalyst, as discussed in an earlier publication [2]. Overall, ethane addition results in a lower deposits-downstream yield, as shown in SI Figure 7b.

Coke-on-catalyst as well as deposits-downstream are calculated according to the following equations: The total carbon-to-products selectivity is the summation of the selectivity to all GC-measured products.

$$S_C = \Sigma S_{C_x H_y} \qquad\qquad\qquad \textit{Eq. 1}$$

S_c: total carbon to products selectivity (–)

Integral values of conversion, selectivity and coke deposition are calculated in order to compare with data on the amount of deposits on the catalyst after a full experiment as measured with TGA. Equation 5 is used to calculate the total amount of carbon converted in the full experiment:

$$C_{converted\ CH_4} = \int_{t=0}^{t=14h} \phi_{CH_4 in} \cdot \xi_{CH_4} \cdot \frac{1}{V_m} \qquad\qquad \textit{Eq. 2}$$

ϕ_x: flow of x $(ml \cdot s^{-1})$
V_m: molar volume at SPT $(ml \cdot mol^{-1})$

The total amount of carbon that is converted to deposits during an integral experiment is calculated based on the difference in mass-balance closure as presented in Eq. 6:

$$C_{deposits-downstream} = \int_{t=0}^{t=14h} \phi_{CH_4 in} \cdot \xi_{CH_4} \cdot (1-S_c) \cdot \frac{1}{V_m} \qquad \textit{Eq. 3}$$

Deposits can form either on the catalyst, named 'coke-on-catalyst' or down-stream of the catalyst-bed on the reactor-wall or in the tubing to the GC, named 'deposits-downstream'. The amount of coke formed on the catalyst during a full experiment is also be calculated based on the weight loss during oxidation of the spent catalyst in TGA, according to equation 7, assuming coke-on-catalyst contains exclusively C:
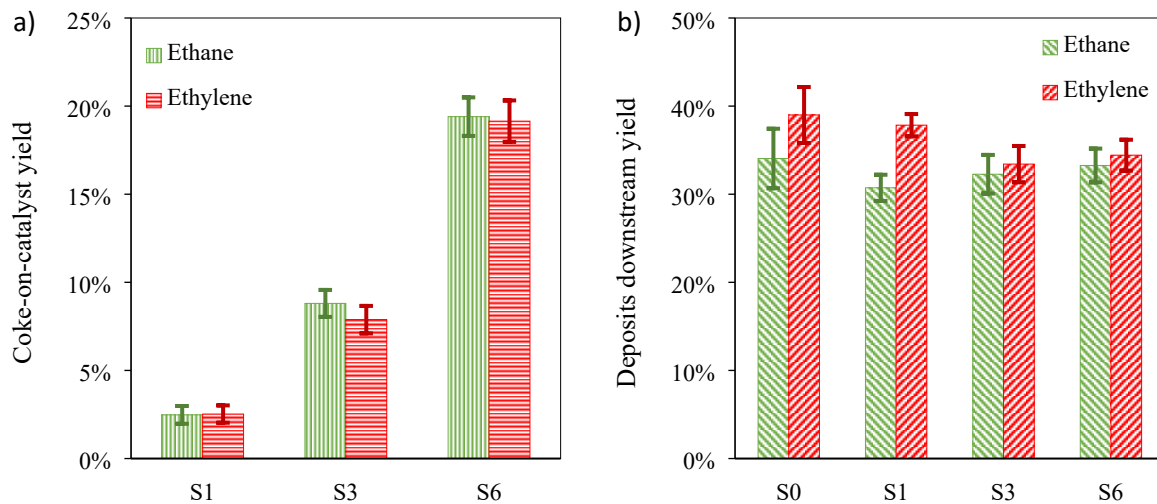
$$C_{coke-on-catalyst} = \Delta W_{TGA} \cdot \frac{Q_{cat}}{M_C} \qquad\qquad \textit{Eq. 4}$$

M_C: molar mass of carbon $(g \cdot mol^{-1})$
ΔW_{TGA}: the percentage of mass decrease in the TGA analysis (–)
Q_{cat}: amount of catalyst in the reactor (g)

Deposits-downstream include a wide array of poly aromatic hydrocarbons of C_{10+} in carbon number, as well as coke deposited on the reactor-wall downstream of the catalyst, as presented in a previous work [2].

SI Figure 7: (a) the yield of coke-on-catalyst during a complete experiment as described in the text and (b) the yield of deposits formed downstream of the catalyst assuming a closing mass balance. Reactor temperature 1000°C; pre-heater and post-heater operated at 400 °C; 90% CH_4 in N_2. Complete experiment during 8h, varying ethane or ethylene concentration between 0 and 2.5%;

S.4   The average composition of natural gas in the US gulf-coast

SI Table 1: The composition of US gulf-coast natural gas according to [3].

Component	Mole fraction (%)	Trace components	Amount
N_2	1.25	S-components	5.5 mg·m^{-3}
CH_4	91.01	H_2O	<65 mg·m^{-3}
C_2	4.88	O_2	0.01 mole%
C_3	1.69	CO_2	0.01 mole%
C_4	0.66		
C_5	0.27		
C_6	0.13		
C_7 and above	0.11		

References

1. X. Bao, personal communication.
2. R. S. Postma and L. Lefferts, *ChemCatChem*, 2020, DOI: 10.1002/cctc.202001785.
3. Uniongas, Chemical Composition of Natural Gas, https://www.uniongas.com/about-us/about-natural-gas/chemical-composition-of-natural-gas).