Influence of hydrocarbon feed additives on the high-temperature pyrolysis of methane in molten salt bubble column reactors
Supplementary Information

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1. Differential kinetic model

The rate of methane consumption can be expressed using the following simplified rate equation:

$$\frac{d[CH_4]}{dt} = -k_f[CH_4]^n + k_r[H_2]^m \tag{1}$$

Using reaction conditions that result in <10% conversion of methane, the initial concentration of methane is substituted, the differential is expressed as a difference, and back reactions are ignored in the following preliminary model:

$$\frac{\Delta[CH_4]}{\Delta t} = -k_f[CH_4]^{0n} \tag{2}$$

The order in methane (i.e., n) is confirmed to be 1 by measuring the rate of methane consumption versus methane partial pressure at low conversions, where the concentration of methane is calculated using an ideal gas law assumption:

$$[CH_4] = \frac{P_{CH_4}}{RT} \tag{3}$$

By dividing both sides of Equation S2 by the initial concentration (or pressure) of methane, the rate constant, k_f, can now be expressed using only the fractional conversion of methane (X_{CH4}) and the residence time (tau):

$$\frac{X_{CH_4}}{\tau} = -k_f \tag{4}$$

Once k_f has been calculated for each temperature, the Arrhenius expression can be used to find the effective kinetic parameters:

$$k = k^0 e^{-\frac{E_a}{RT}} \tag{5}$$

$$\ln k = \ln k^0 - \frac{E_a}{RT} \tag{6}$$

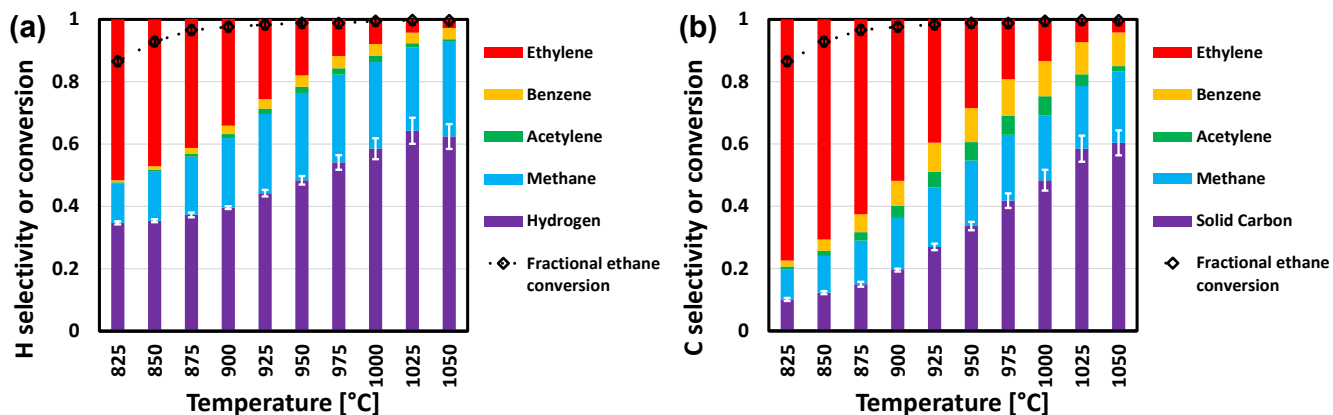## 2. Selectivity of products from hydrocarbon decompositions

Figure S1: Fractional ethane conversion and product selectivity on (a) a H basis and (b) a C basis as a function of temperature. 3 SCCM of ethane and 12 SCCM of argon are bubbled through 18 cm of molten KCl with an estimated bubble residence time of ~0.75 seconds. 30 SCCM of argon is delivered to the headspace as a sweeping gas.

Figure S2: Fractional propane conversion and product selectivity on (a) a H basis and (b) a C basis as a function of temperature. 3 SCCM of propane and 12 SCCM of argon are bubbled through 18 cm of molten KCl with an estimated bubble residence time of ~0.75 seconds. 30 SCCM of argon is delivered to the headspace as a sweeping gas.
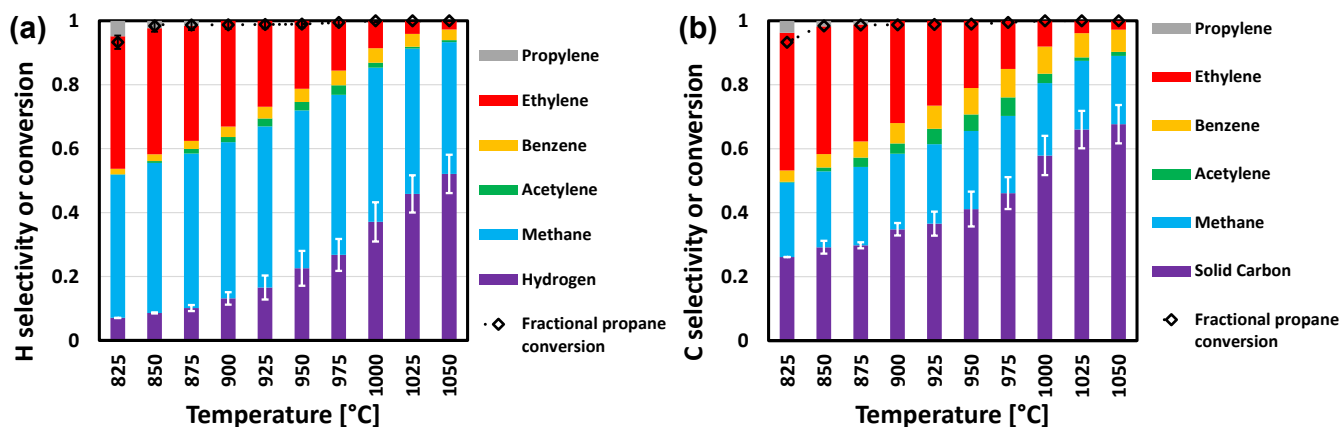
Figure S3: Fractional butane conversion and product selectivity on (a) a H basis and (b) a C basis as a function of temperature. 3 SCCM of butane and 12 SCCM of argon are bubbled through 18 cm of molten KCl with an estimated bubble residence time of ~0.75 seconds. 30 SCCM of argon is delivered to the headspace as a sweeping gas.
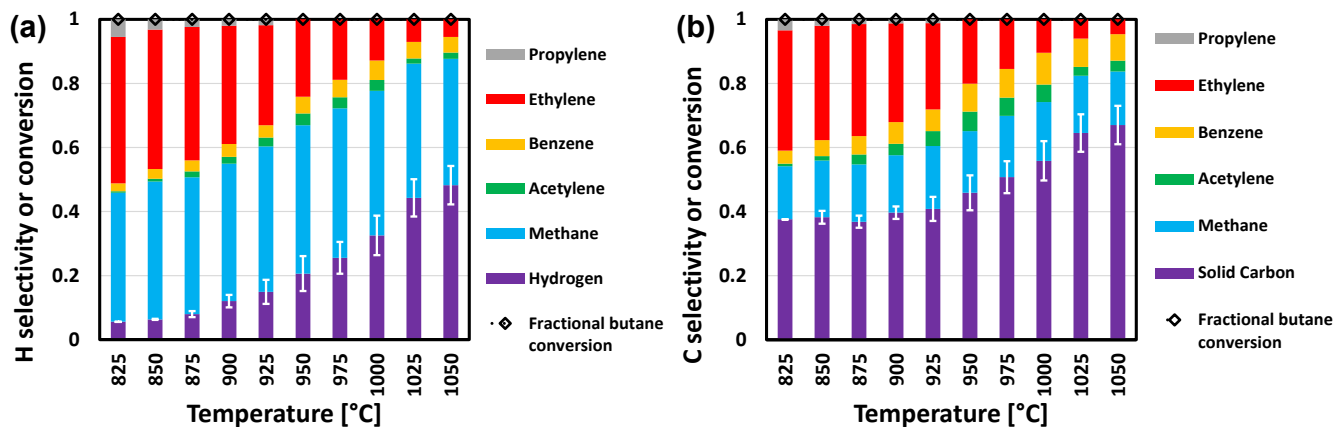

Figure S4: Fractional acetylene conversion and product selectivity on (a) a H basis and (b) a C basis as a function of temperature. 3 SCCM of acetylene and 12 SCCM of argon are bubbled through 18 cm of molten KCl with an estimated bubble residence time of ~0.75 seconds. 30 SCCM of argon is delivered to the headspace as a sweeping gas.
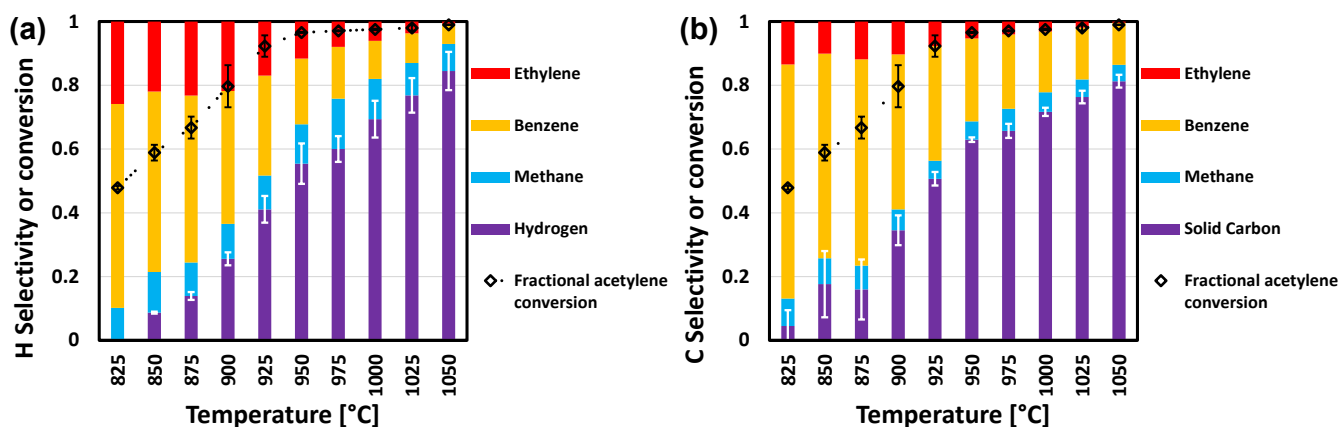
Figure S5: Fractional benzene conversion and product selectivity on a H basis as a function of temperature. 1.5 SCCM of benzene and 15 SCCM of argon are bubbled through 18 cm of molten KCl with an estimated bubble residence time of ~0.75 seconds. 30 SCCM of argon is delivered to the headspace as a sweeping gas.
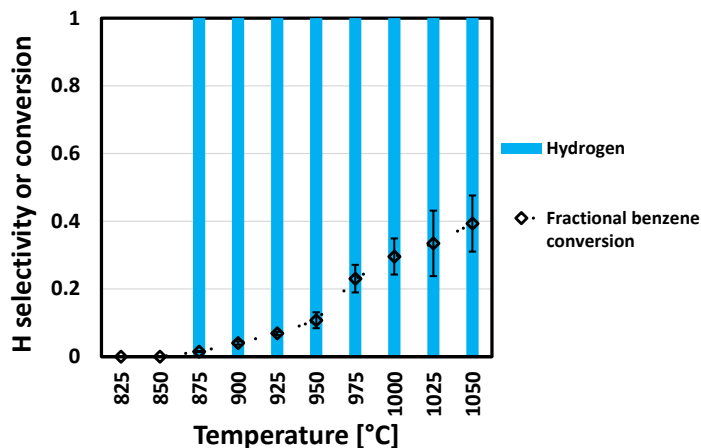
The selectivity of products on a hydrogen basis from hydrocarbon decomposition is calculated by dividing the total amount of atomic hydrogen in a gas product by the total amount of atomic hydrogen that enters the reactor in the hydrocarbon feed. The selectivity on a carbon basis is calculated in similar manner; the missing carbon that is not accounted for in gaseous products is assumed to be present in solid carbon. Although, some carbon (and hydrogen) may also be present in larger aromatic molecules that deposit in the headspace of the reactor.

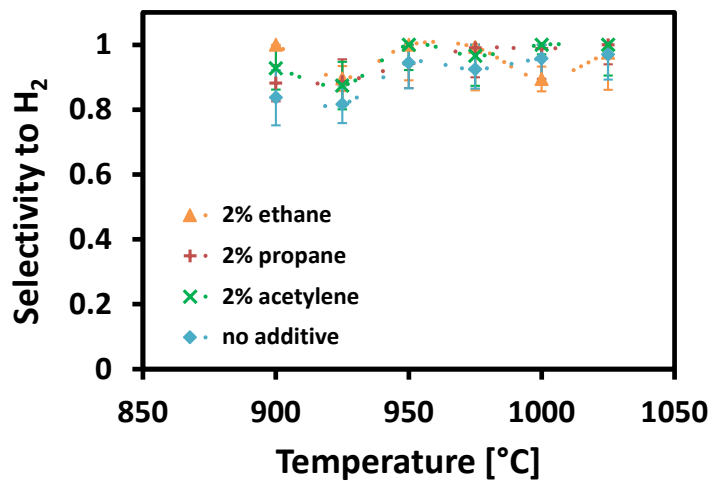# 3. Methane product selectivity with and without feed additives

Figure S6: H_2 selectivity of gaseous products of methane pyrolysis (MP) with and without +2% of select hydrocarbon feed additives in a molten KCl bubble column. 15 SCCM of gas is bubbled into the melt at a depth of 18 cm with an approximated bubble residence time of ~0.75 seconds. 30 SCCM of argon is introduced in the headspace of the reactor for quantitative product analysis and to minimize reactions in the headspace.

4. Effective kinetic parameters of MP with hydrocarbon feed additives

Table S1: Effective first-order kinetic parameters (pre-exponential factors and activation energies) for k_2 measured using differential methane conversion conditions.

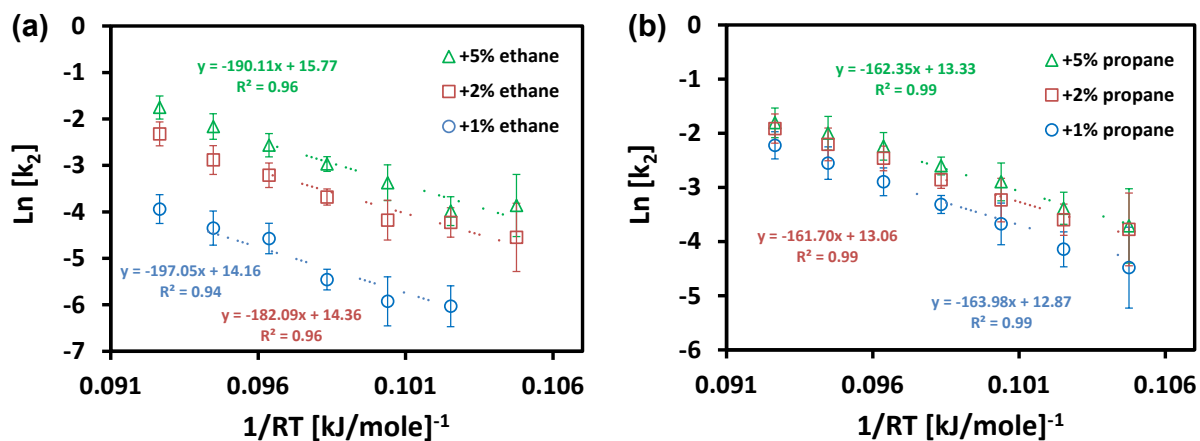| Feed additive	k_{0_2} [1/s]	Ea_2 [kJ/mole]
1% ethane	1.4×10^6	197
2% ethane	1.7×10^6	182
5% ethane	7.1×10^6	190
1% propane	3.9×10^5	164
2% propane	4.7×10^5	162
5% propane	6.1×10^5	162
2% butane	2.8×10^3	104
2% acetylene	3.3×10^6	182

Figure S7: Arrhenius plots using calculated k_2 values for +1%, +2%, and +5% of (a) ethane and (b) propane hydrocarbon feed additives to methane pyrolysis in a molten KCl bubble column. Data points used are for differential methane conversions.

5. Scale-up calculations for industrial reaction rates

The equation used to calculate the best-case scenario initial rates of methane decomposition in industrial bubble column reactors is as follows:

$$rate\left[\frac{mol}{m_{reactor}^3\,s}\right] = \varepsilon\left[\frac{m_{gas}^3}{m_{reactor}^3}\right] * k(T)\left[\frac{1}{s}\right] * \frac{P_{CH_4}}{RT}\left[\frac{mol}{m_{gas}^3}\right]$$

(7)

Here, ε is the gas holdup.

For an industrial steam methane reformer, a first-order approximation for the overall rate of reaction (assuming 100% conversion of methane to products) can be calculated using the following:

$$rate\left[\frac{mol}{m^3-s}\right] = \frac{1}{\tau}\left[\frac{1}{s}\right] * \frac{P_{CH_4}}{RT}\left[\frac{mol}{m^3}\right]$$

(8)

Here, tau is the residence time. Assuming methane partial pressures of 10–15 atm and a residence time of 1–3 seconds, the overall rates are ~32–143 mol/m^3-s at 1000 °C in industrial reactors such as those is SMR processes. At 1 atm (assuming a first-order reaction), the resultant rates are approximately 3–10 mol/m^3-s. Therefore, we use a more conservative estimate of 1 mol/m^3-s as a target rate at 1 atm.

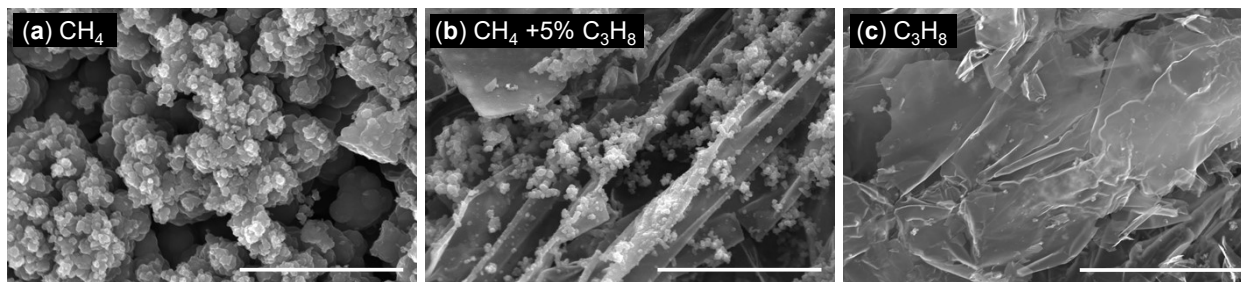## 6. Supplemental Scanning Electron Microscopy (SEM) images

Figure S8: SEM images of the carbon synthesized in a molten KCl bubble column reactor at 1000 °C and 1 atm using different hydrocarbon feedstocks: (a) 15 SCCM CH$_4$; (b) 15 SCCM CH$_4$ + 0.75 SCCM C$_3$H$_8$; and (c) 3 SCCM C$_3$H$_8$ + 12 SCCM Ar. All carbons have been washed with 70 °C water for two hours with constant stirring. Scale bars in all images correspond to 10 μm.
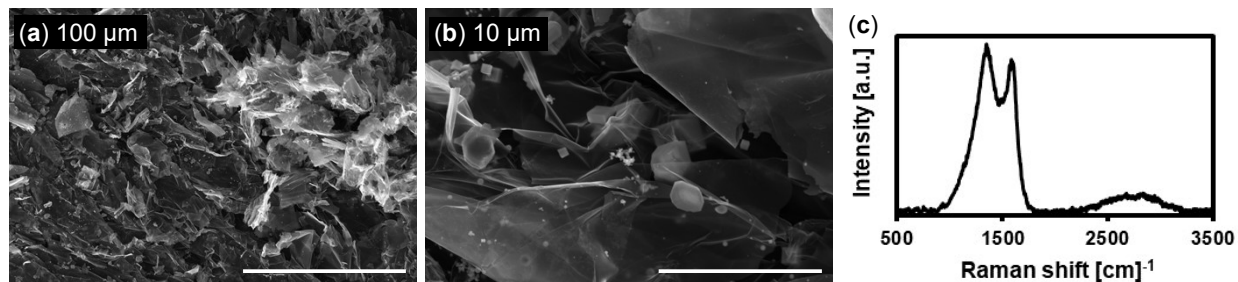
7. Benzene pyrolysis in molten KCl

Figure S9: (a-b) SEM images and (c) Raman spectrum of the carbon product synthesized in a molten KCl bubble column reactor at 1000 °C and 1 atm using 0.09 atm of benzene supplemented with 0.91 atm of argon. Carbon product has **_not_** been washed with hot water. (a) 100 μm scale bar and (b) 10 μm scale bar.

Table S1: EDX analysis of solid carbon produced in a molten KCl bubble column reactor at 1000 °C and 1 atm from different hydrocarbon feedstocks. Carbon products have **_not_** been washed using hot water.

Feedstock	Weight [%]		
	K	Cl	C
CH_4	27.5 ± 1.5	25.1 ± 1.2	47.4 ± 2.7
C_6H_6	8.5 ± 0.5	7.2 ± 0.4	84.3 ± 0.9
C_3H_8	4.0 ± 0.2	4.7 ± 0.2	91.3 ± 0.4