Electronic Supplementary Material (ESI) for RSC Advances.

C to H effective ratio as a descriptor for co-processing light oxygenates and CH_4 on Mo/H-ZSM-5

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Supplementary Information

Figure S.1 depicts the time-on-stream dependence of measured C_6H_6 synthesis for or CH_4, CH_4/acetic acid, CH_4/H_2O, and CH_4/methanol co-feed experiments at 950 K and 1.0 g Mo/H-ZSM-5.

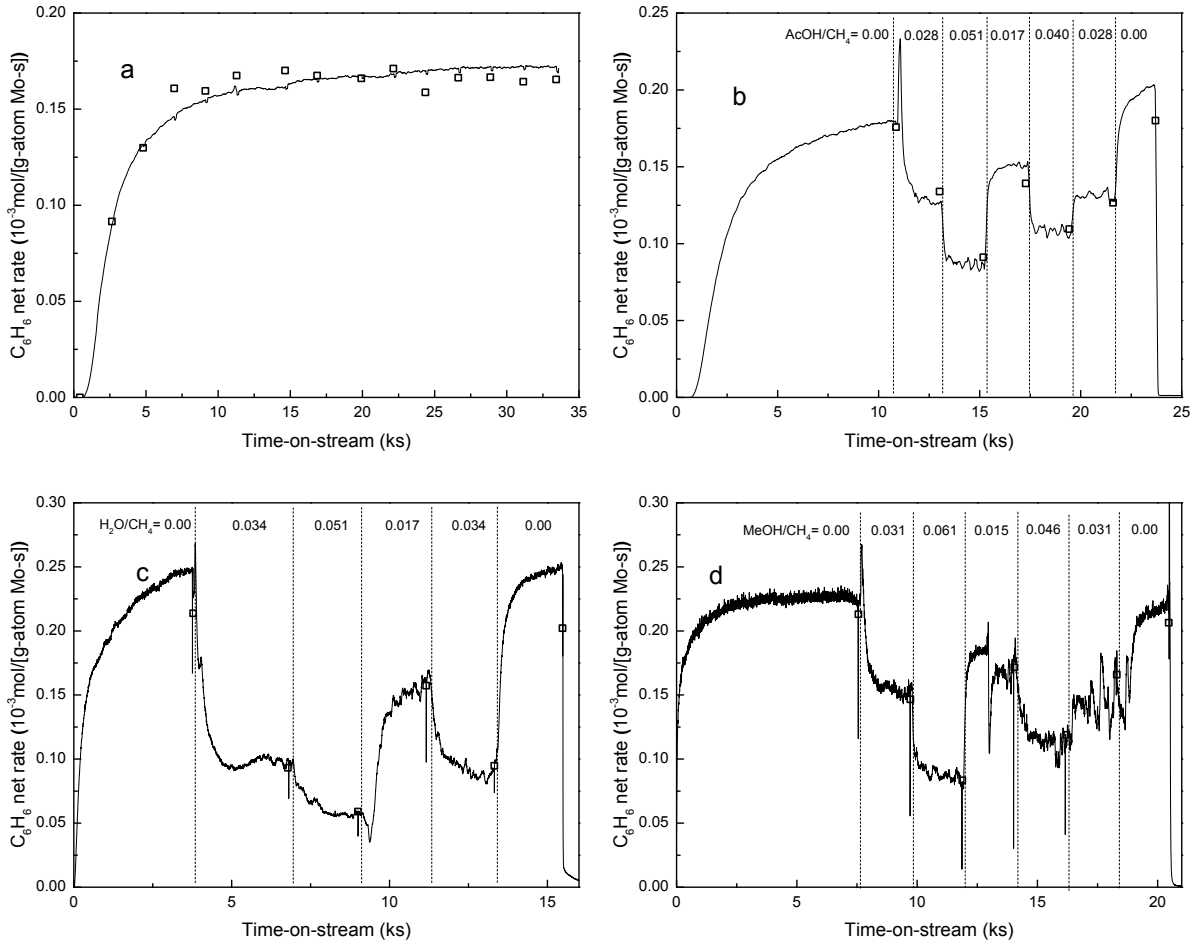

Figure S.1 C_6H_6 (□) net synthesis rates at 950 K, CH_4 flow rate 12.0 cm^3 min^{-1}, CH_4:Ar = 9:1, catalyst loading 1000 mg with Mo:Al_f = 0.25. Symbols are GC data and solid lines are MS transient data. a) CH_4 only, b) CH_4/AcOH, c) CH_4/H_2O, and d) CH_4/MeOH.

Figure S.2 depicts thermodynamic equilibrium amounts of hydrocarbons and oxygenates with a starting composition of 1 kmol CH_4 and 0.1 kmol CH_3COOH as a function of temperature (273 – 1073 K).

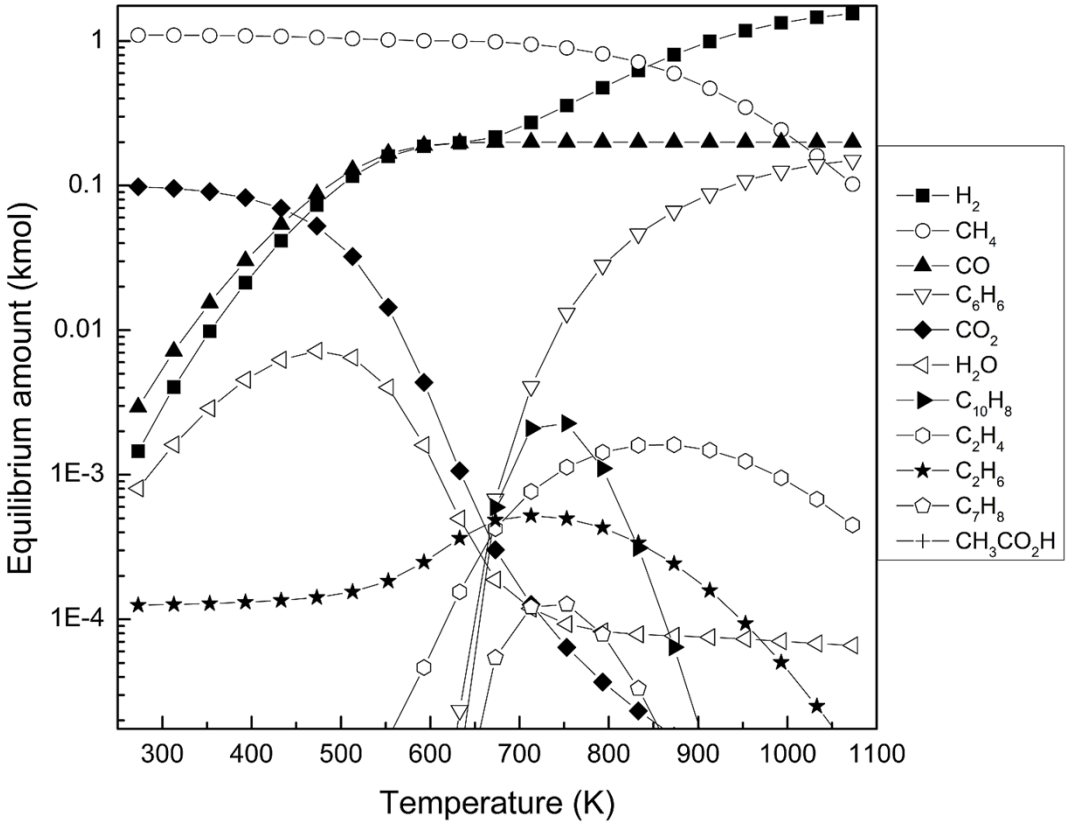

Figure S.2 Equilibrium amounts of hydrocarbons and oxygenates as a function of temperature starting as CH_4 (1 kmol) and CH_3COOH (0.1 kmol).

Figures S.3a and S.3b depict CO production as the sole oxygen-containing product when processing H_2O/CH_4 at various ratios. CO_2 and H_2O mass spectrometric signals are 1-2 orders of magnitude lower than that for CO.

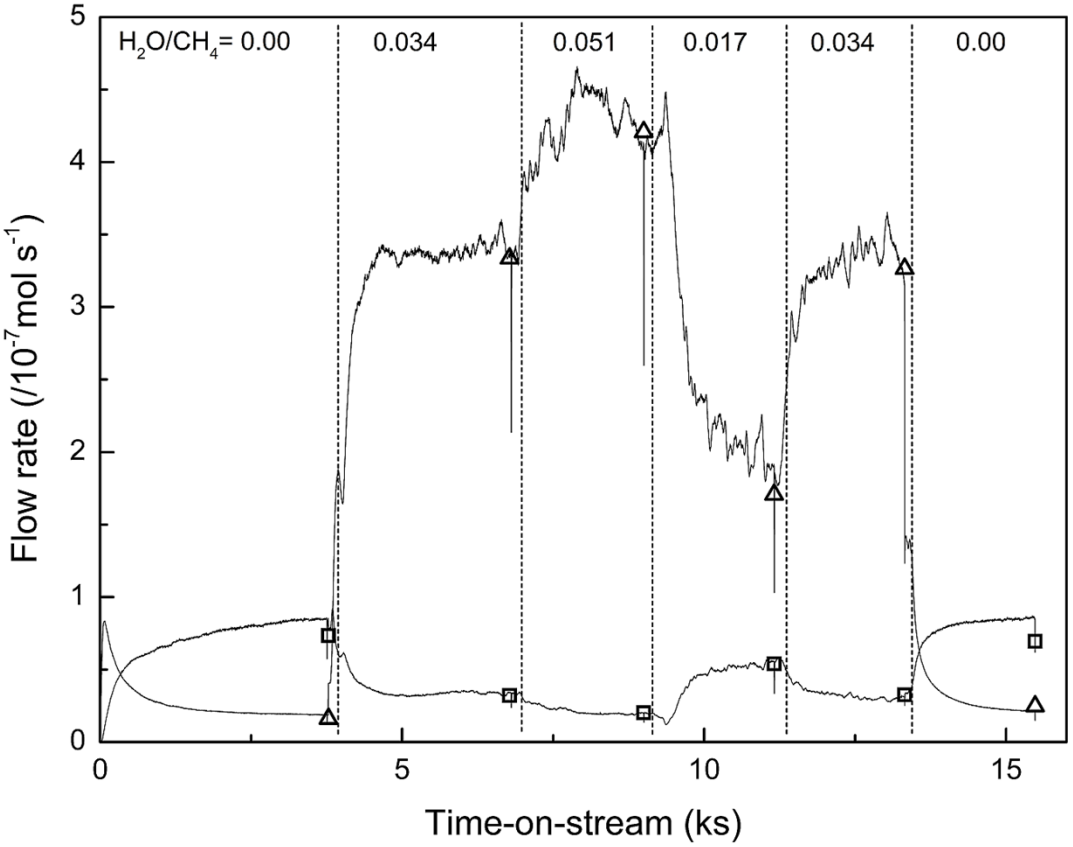

Figure S.3a C_6H_6 (□) and CO (❒) molar flow rates at 950 K, CH_4 flow rate 12.0 cm^3 min^{-1}, CH_4:Ar = 9:1, catalyst loading 1000 mg with $Mo:Al_f = 0.25$. Inlet H_2O/CH_4 ratio = 0.00, 0.034, 0.051, 0.017, 0.034, and 0.00. Symbols are GC data and solid lines are MS transient data.

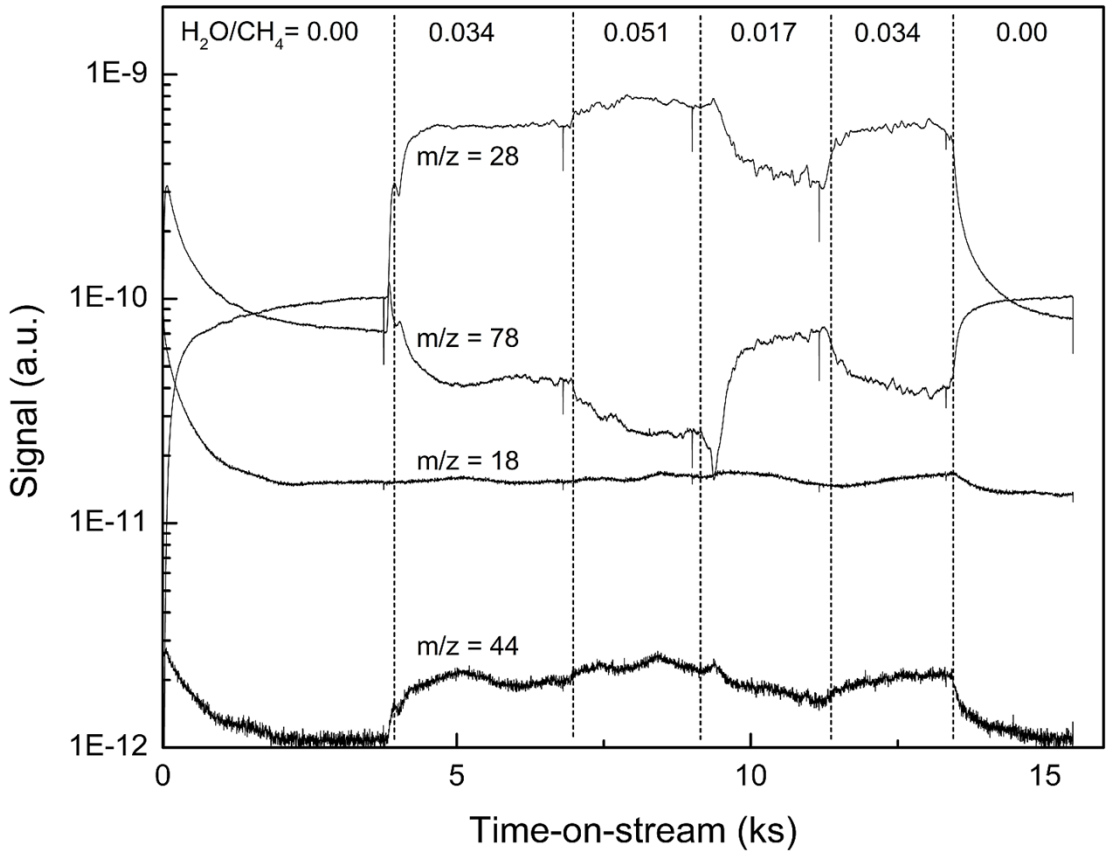

Figure S.3b CO (28), C_6H_6 (78), H_2O (18), and CO_2 (44) mass spectrometry signals at 950 K, CH_4 flow rate 12.0 $cm^3\ min^{-1}$, CH_4:Ar = 9:1, catalyst loading 1000 mg with Mo:Al_f = 0.25. Inlet H_2O/CH_4 ratio = 0.00, 0.034, 0.051, 0.017, 0.034, and 0.00. Symbols are GC data and solid lines are MS transient data.

Figure S.4 depicts the outlet CO flow rate at various H_2O inlet flow rates.

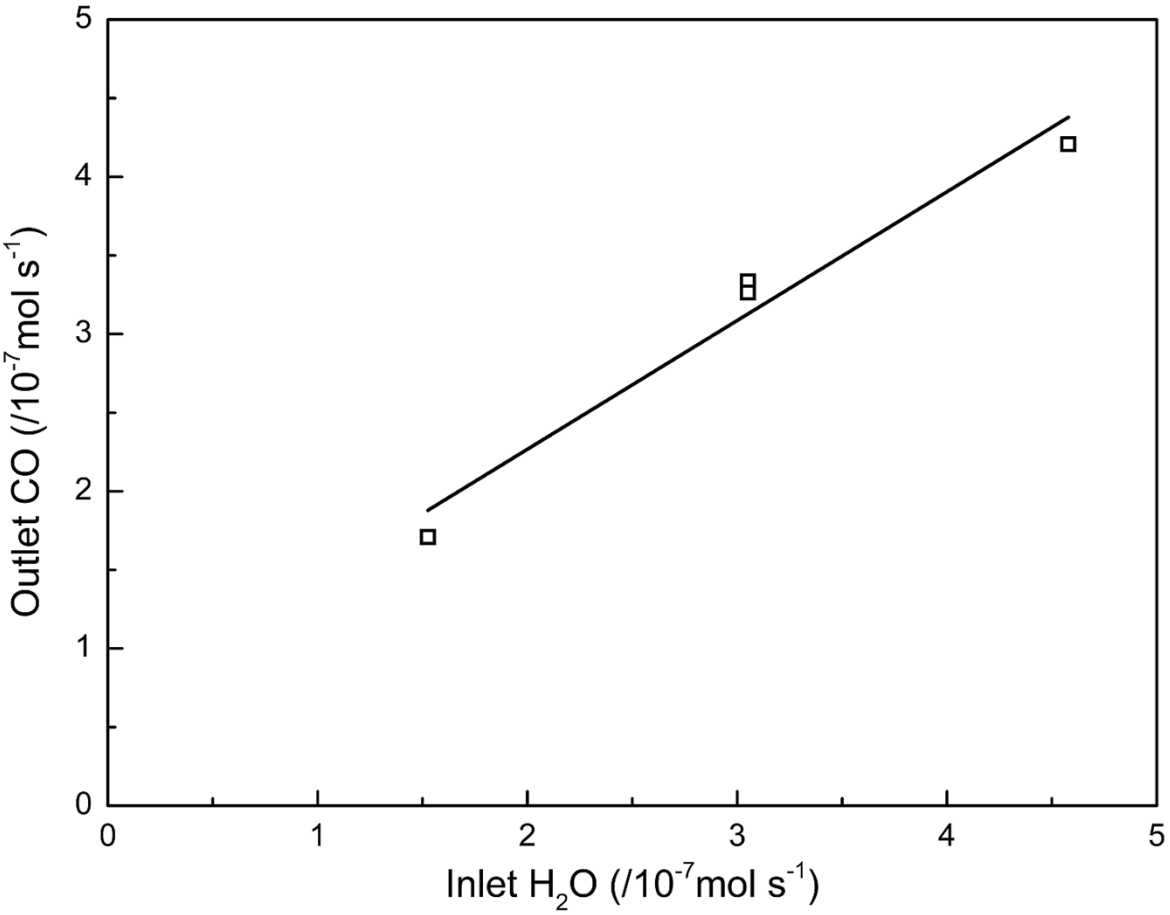

Figure S.4 Outlet CO flow rate as a function of inlet H_2O flow rate.

Figure S.5 depicts total hydrocarbon (sum of C_2H_4, C_2H_6, C_6H_6, C_7H_8, and $C_{10}H_8$) net synthesis rate as a function of the feed C/H_{eff}. Net rates are calculated based on total catalyst loaded (1.0 g) and not adjusted for Mo oxidation.

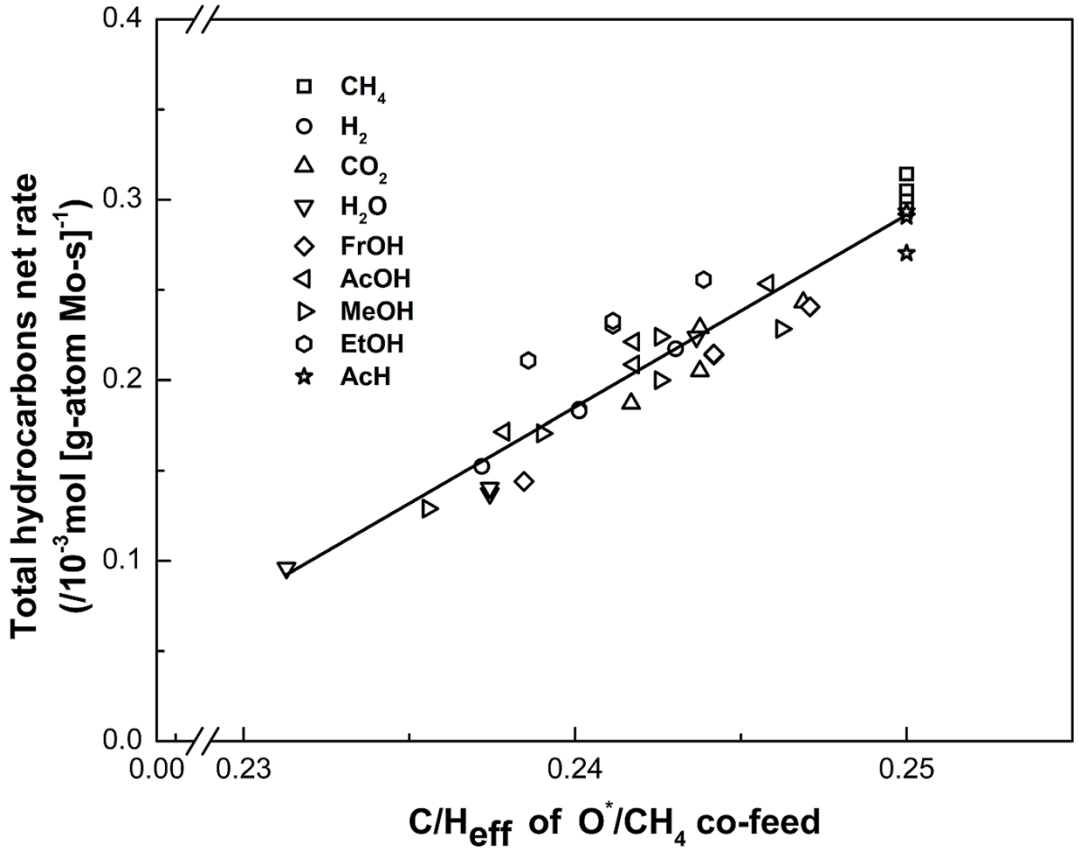

Figure S.5 Total hydrocarbon net synthesis rate as a function of C/H_{eff} at 950 K, CH_4 flow rate 12.0 cm^3 min^{-1}, CH_4/Ar = 9:1, catalyst weight 1.0 g with Mo/Al_f =0.25, and H_2/CH_4 = 0.057-0.108, CO_2/CH_4 = 0.012-0.033, H_2O/CH_4 = 0.017-0.051, $FrOH/CH_4$ = 0.008-0.031, $AcOH/CH_4$ = 0.017-0.051, $MeOH/CH_4$ = 0.015-0.061, $EtOH/CH_4$ = 0.053-0.106, or AcH/CH_4 = 0.055-0.110.

The tabulated results presented in Table S.1 show the observed product distribution and conversion for co-processing oxygenate/CH_4 mixtures at 950 K.

Table S.1 CH_4 conversion and hydrocarbon product selectivity for DHA reactions over Mo/H-ZSM-5 catalyst at 950 K, CH_4 flow rate 12.0 cm^3 min^{-1}, CH_4:Ar = 9:1, catalyst loading 1 g with Mo:Al_f = 0.25, and time-on-stream 13 ks.

Co-feed	CH_4	H_2	CO_2	H_2O	FrOH	AcOH
O*/CH_4	-	0.082	0.033	0.034	0.016	0.034
CH_4 conversion (%)[a]	7.3	4.7	6.0	4.4	6.0	4.0
Selectivity (%)[b]						
C_2H_4	2.0	2.7	2.7	2.5	2.2	2.2
C_2H_6	1.8	3.2	2.9	4.1	2.9	2.3
C_6H_6	70.8	71.5	71.2	70.8	71.6	70.7
C_7H_8	3.4	3.2	3.3	3.0	3.4	3.1
$C_{10}H_8$	21.0	18.2	18.5	18.3	17.9	20.5

[a] $Conv_{CH_4} = \frac{F_{CH_4}^{Inlet} - F_{CH_4}^{Outlet}}{F_{CH_4}^{Inlet}}$ [b] $\%S_i = \frac{n_i * F_i}{\sum_i n_i * F_i}$