Supporting information

Elucidating the reaction pathway for ethene and propene formation in methanol to hydrocarbons reaction over high silica H-Beta

Jie Zhang[ab], Zhihua Huang[ab], Peidong Li[ab], Xiaomin Zhang[a], Xinzhi Zhang[a], Yangyang Yuan[a] and Lei Xu*[a]*

[a] Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, P. R. China;

[b] University of Chinese Academy of Sciences, Beijing 100049, P. R. China.

Table S1. XRF results of H-Beta, HZSM-5, and H-SSZ-13.

Samples	H-Beta	H-ZSM-5	H-SSZ-13
Si/Al	125	132	86

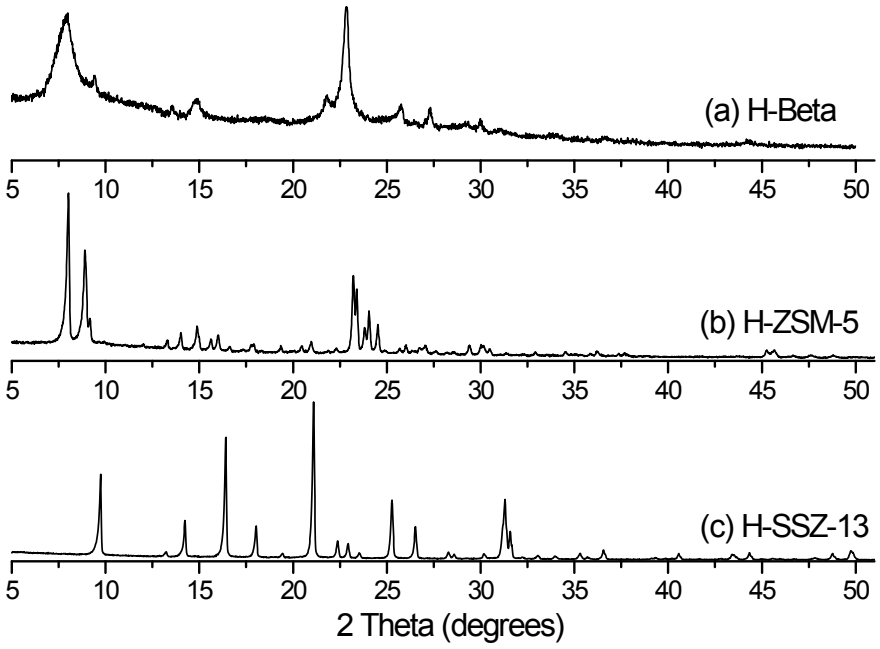

Figure S1. XRD patterns of H-Beta, H-ZSM-5, and H-SSZ-13 samples.

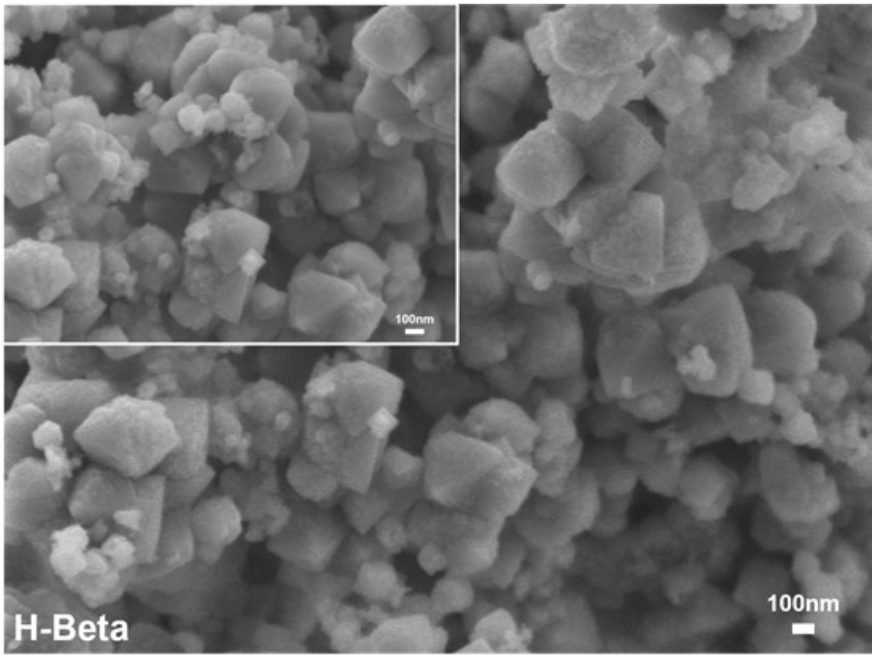

Figure S2-1. SEM images of H-Beta.

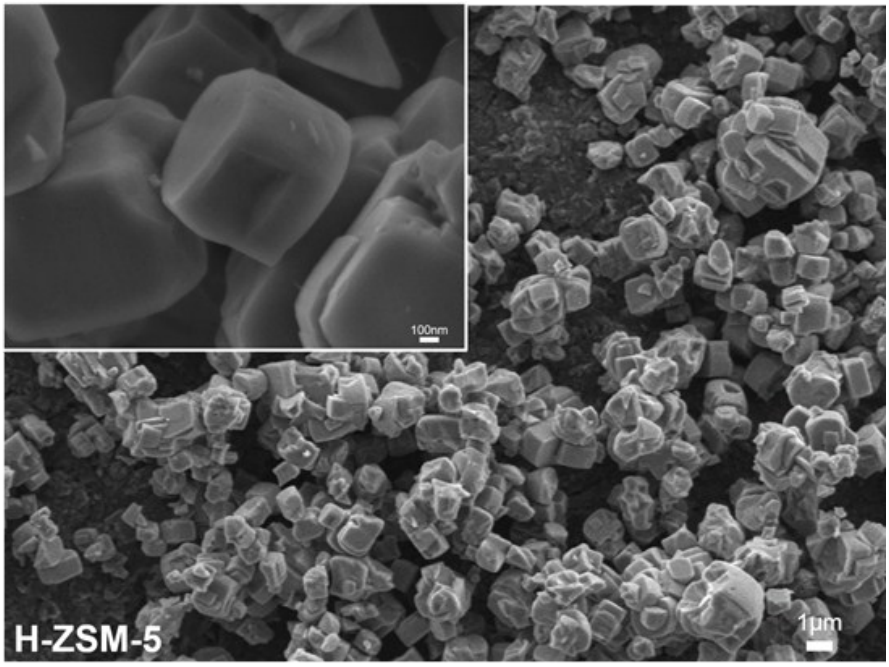

Figure S2-2. SEM images of H-ZSM-5.

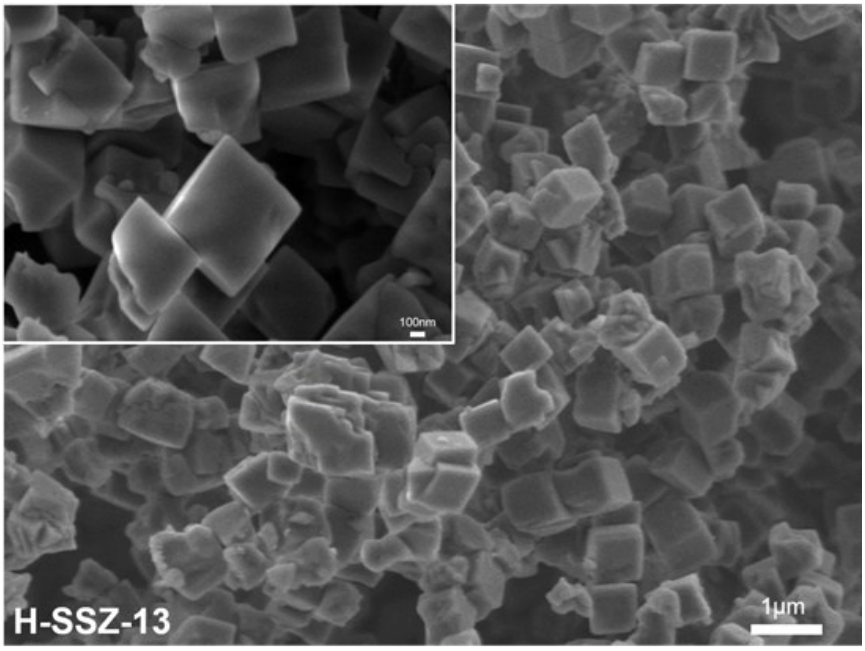

Figure S2-3. SEM images of H-SSZ-13.

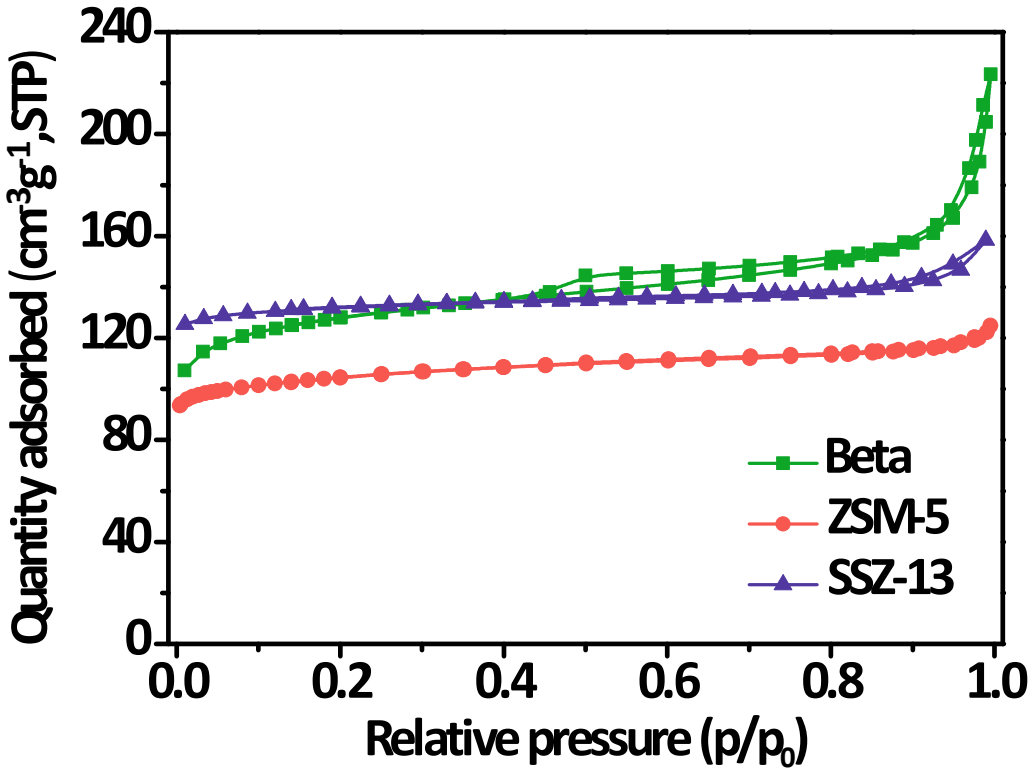

Figure S3. N_2 adsorption-desorption isotherms of H-Beta, H-ZSM-5, and H-SSZ-13.

Table S2. Textural properties of H-Beta, H-ZSM-5, and H-SSZ-13.

Sample	Surface area (m^2g^{-1})			Pore volume (cm^3g^{-1})	
	S_{BET} [a]	S_{micro} [b]	$S_{external}$ [b]	V_{micro} [b]	V_{meso} [c]
H-Beta	419	295	124	0.14	0.19
H-ZSM-5	413	345	68	0.13	0.05
H-SSZ-13	399	363	37	0.19	0.05

[a] Surface area by Brunauer-Emmett-Teller (BET) method. [b] Micropore and external surface area and micropore volume by t-plot method. [c] Mesopore volume by Barrett-Joyner-Hallenda (BJH) method.

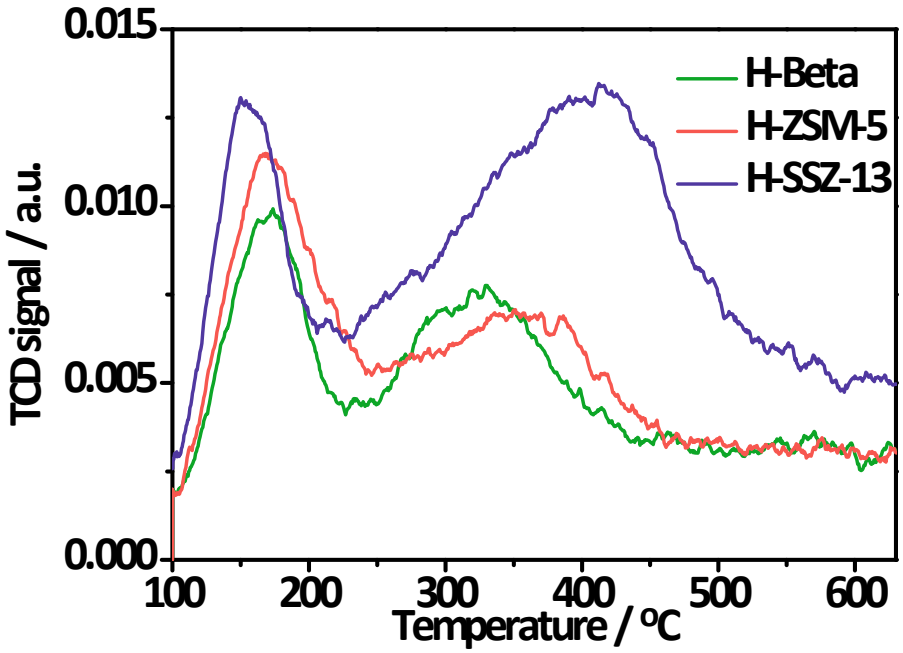

Figure S4. NH_3-TPD spectra of H-Beta, H-ZSM-5, and H-SSZ-13.

Table S3. NH_3-TPD data and acid amount for H-Beta, H-ZSM-5, and H-SSZ-13.

Samples	Si/Al[a]	T_{peak} (°C)		Acid amount[c] (μmol g^{-1})		
		LT peak[b]	HT peak[b]	Total acidity	Weak acidity	Strong acidity
H-Beta	125	168	319	131.4	60.0	71.5
H-ZSM-5	132	167	350	157.1	79.3	77.8
H-SSZ-13	86	153	396	278.3	63.1	215.2

[a] The Silica-to-alumina ratio was obtained by an X-ray fluorescence spectrometer. [b] The LT peak represents a low temperature desorption peak. The HT peak represents a high temperature desorption peak. [c] Calculated with Gaussian function fit.

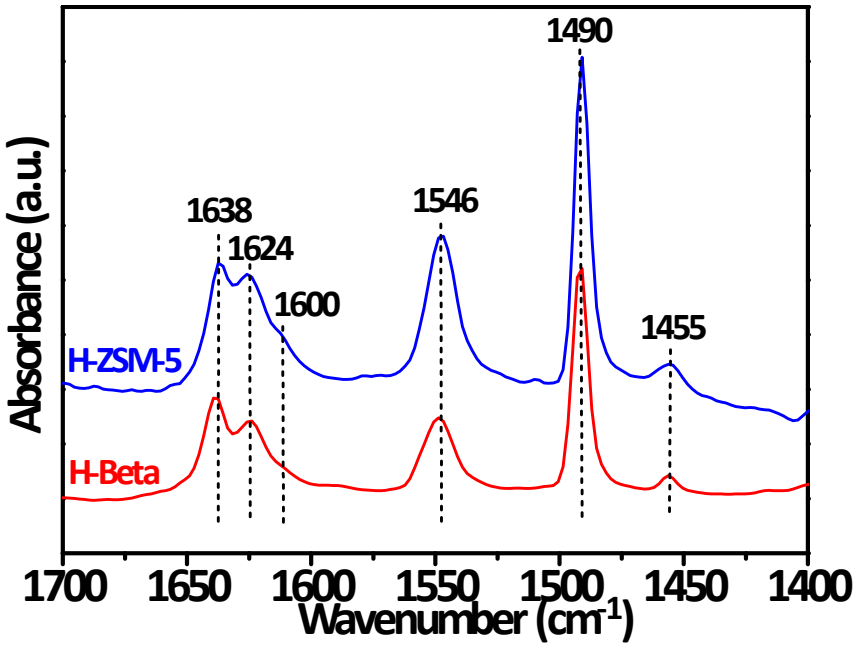

Figure S5. FTIR spectra of pyridine-adsorbed H-Beta, H-ZSM-5.

Table S4. Acidic Properties of H-Beta and H-ZSM-5.

Sample	Acidity by Py-IR (μmol g^{-1}) [a]			
	B/L	Brønsted	Lewis	total
H-Beta	10.8	74.5	6.9	81.4
H-ZSM-5	8.2	90.4	11.0	101.4

[a] The quantities of Brønsted and Lewis acid sites were calculated from the Py-IR spectra.

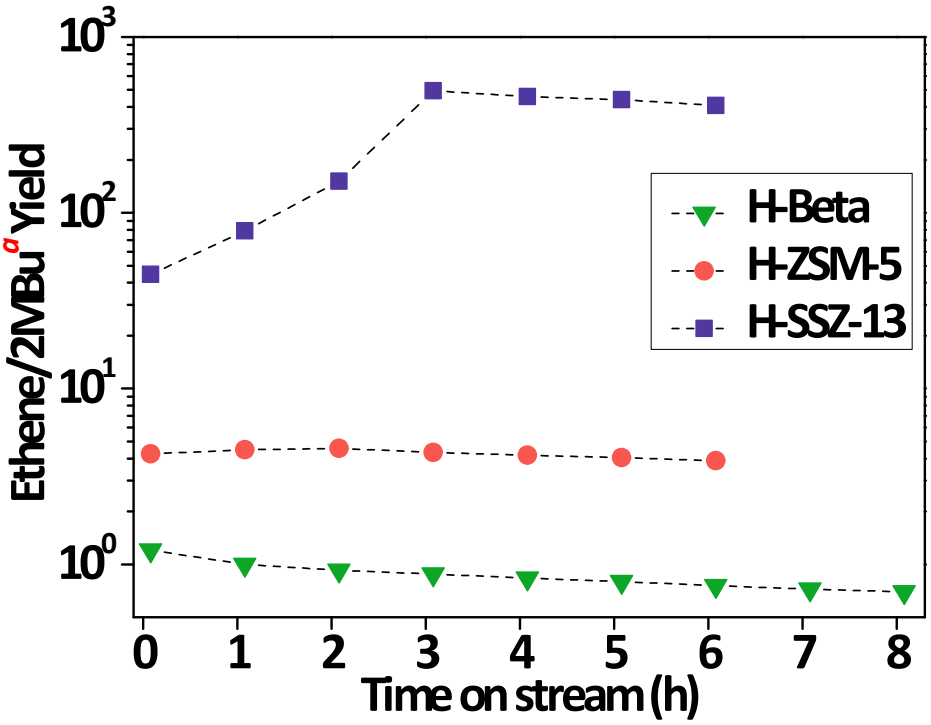

Figure S6. Ethene/2MBu yield versus time on stream over H-Beta, H-ZSM-5, and H-SSZ-13. Reaction condition: T=450 °C; WHSV= 2 h^{-1}; P_{MeOH}= 17 kPa. [a] Ethene/2MBu designates the ratio of the synthesis of ethene and 2-methylbutane + 2-methyl-2-butene.

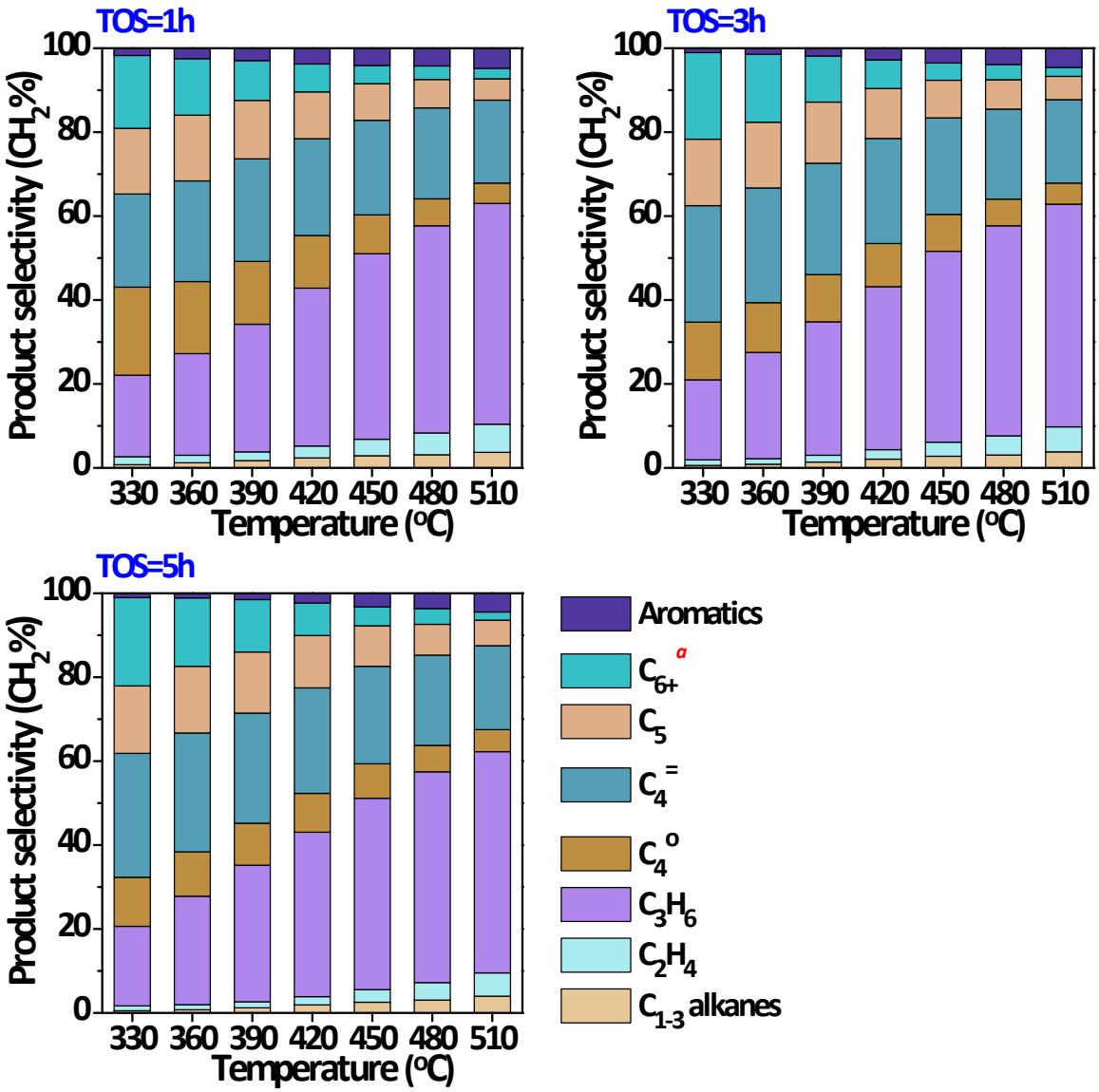

Figure S7. Product selectivities of methanol conversion over H-Beta after 1 h, 3 h, and 5 h on stream at different reaction temperatures. [a] C_{6+} designates all aliphatic hydrocarbons with equal to or greater than six carbon atoms.

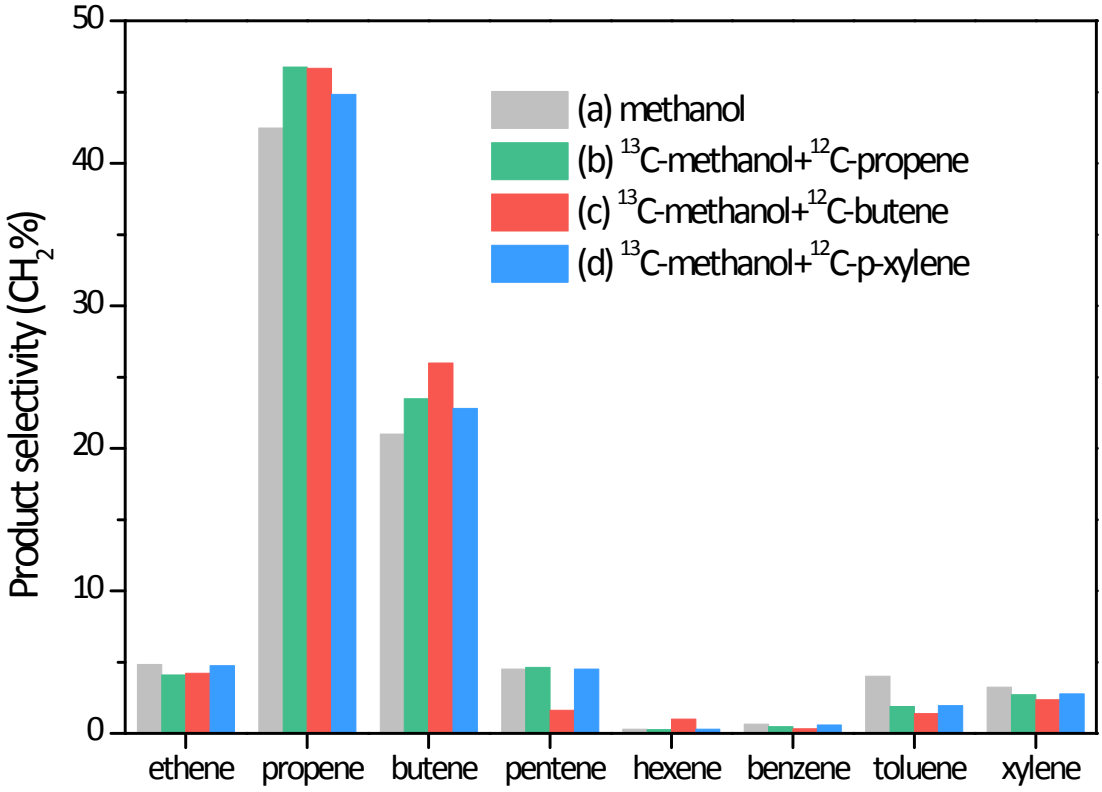

Figure S8. product selectivity after 8min of ^{13}C methanol reaction followed by 2min of ^{13}C methanol co-reaction with ^{12}C-propene, ^{12}C-butene, and ^{12}C-p-xylene over H-beta, H-ZSM-5 and H-SSZ-13 at 450 ^{o}C.

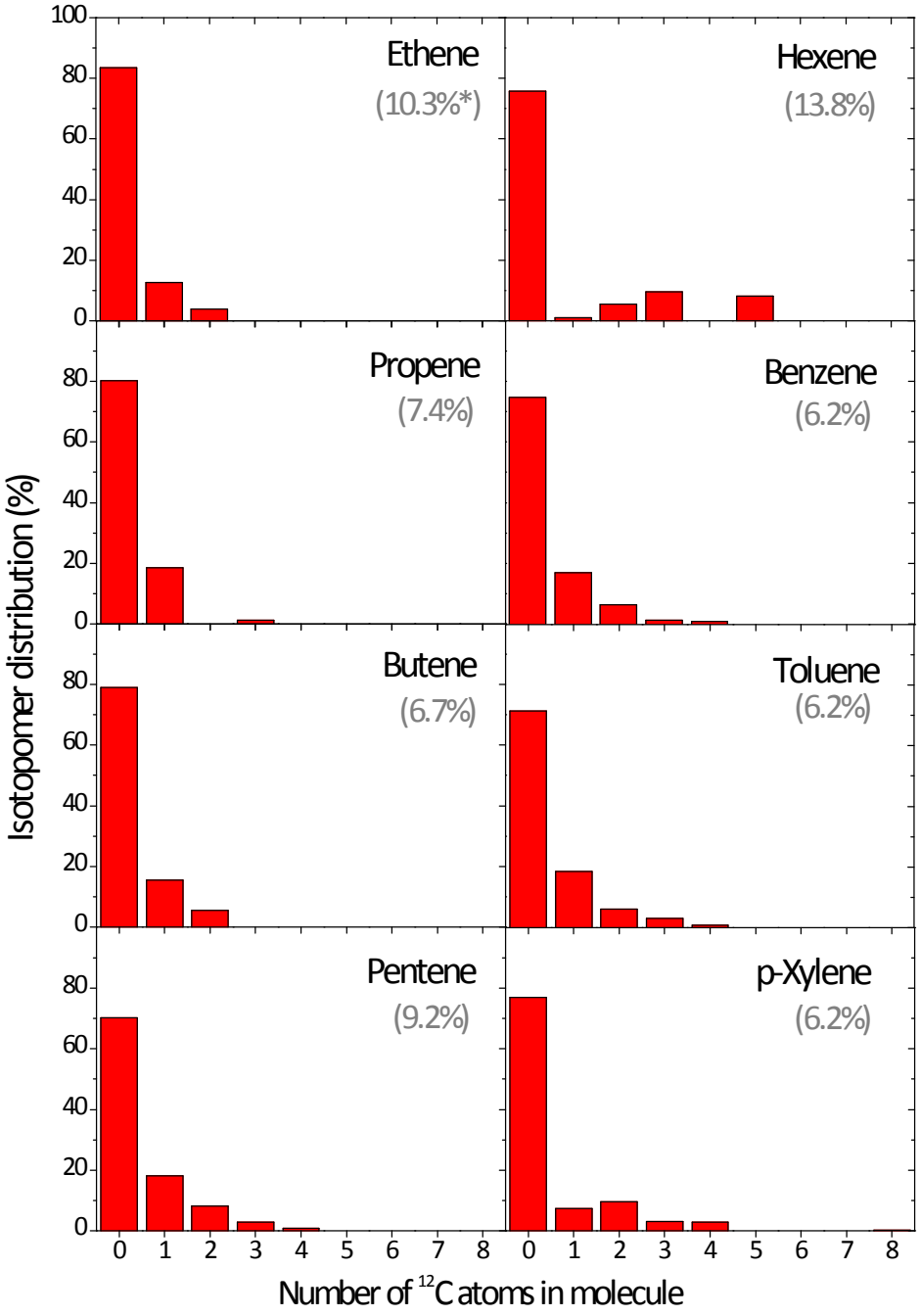

Figure S9-1. Isotopic distributions and total ^{12}C content (number in brackets) in the effluent compounds and retained species after 8min of ^{13}C methanol reaction followed by 2min of ^{13}C methanol co-reaction with ^{12}C-propene over H-beta at 450 ^{o}C.

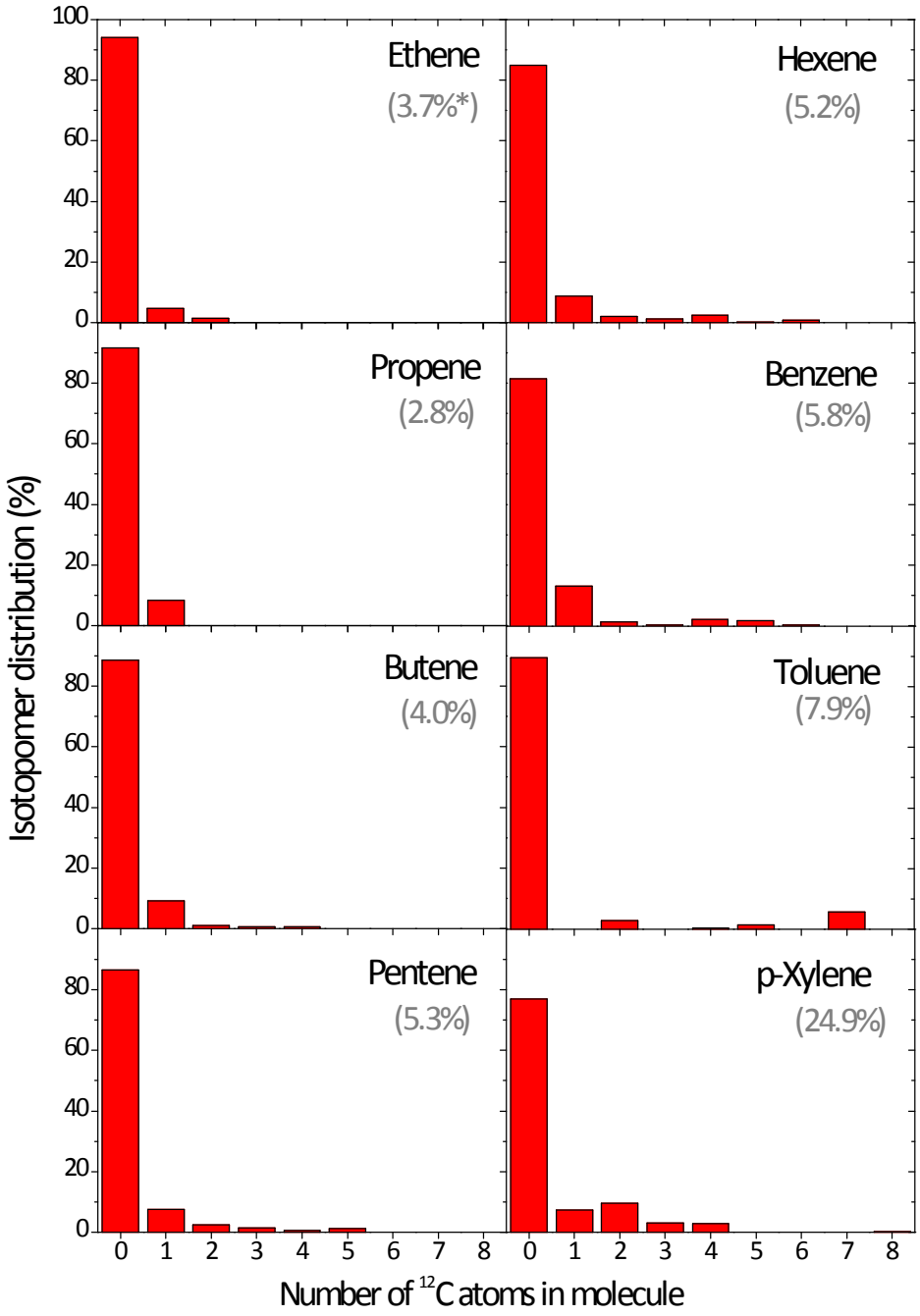

Figure S9-2. Isotopic distributions and total ^{12}C content (number in brackets) in the effluent compounds and retained species after 8min of ^{13}C methanol reaction followed by 2min of ^{13}C methanol co-reaction with ^{12}C-butene over H-beta at 450 ^{o}C.

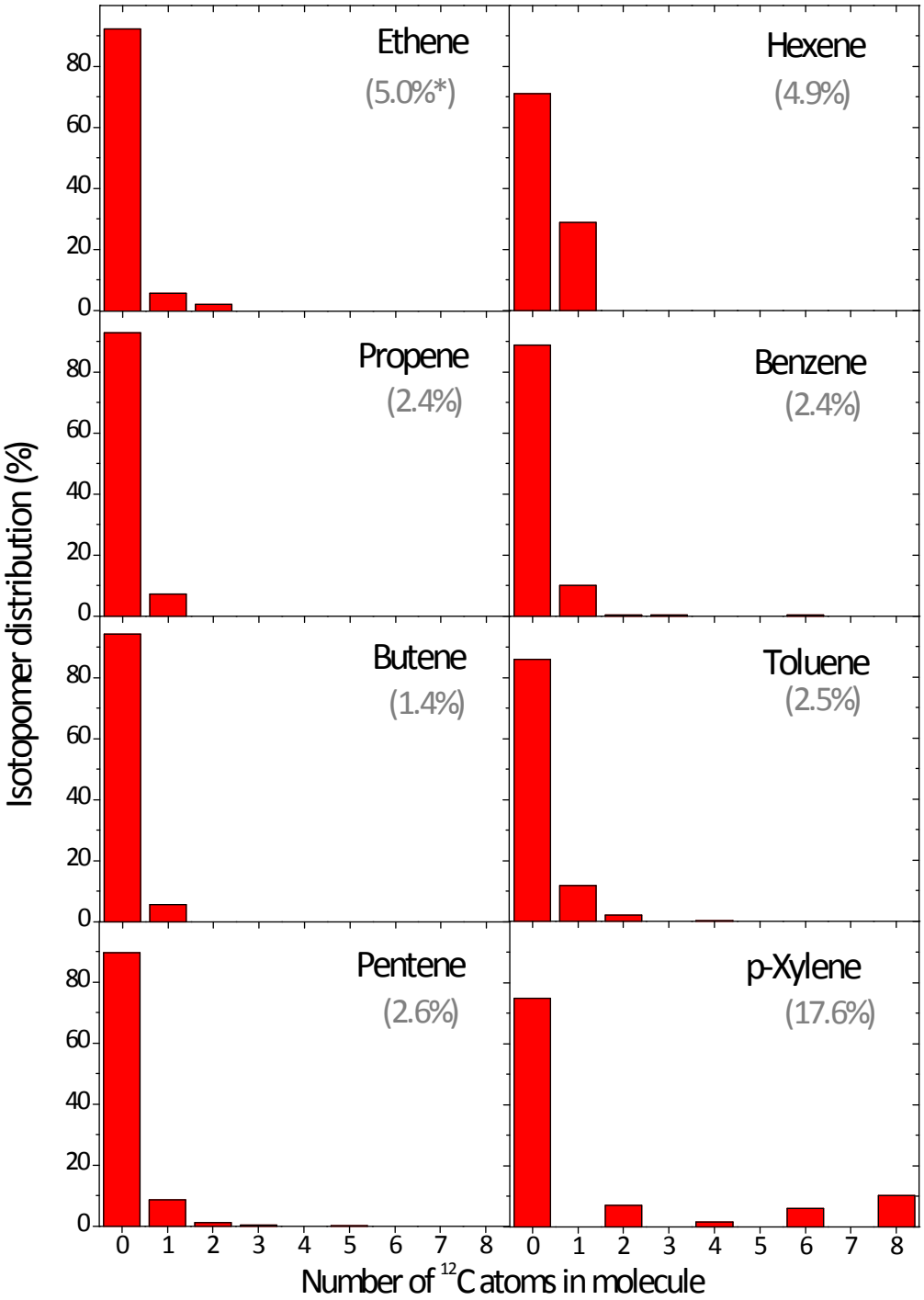

Figure S9-3. Isotopic distributions and total ^{12}C content (number in brackets) in the effluent compounds and retained species after 8min of ^{13}C methanol reaction followed by 2min of ^{13}C methanol co-reaction with ^{12}C-p-xylene over H-beta at 450 ^{o}C.

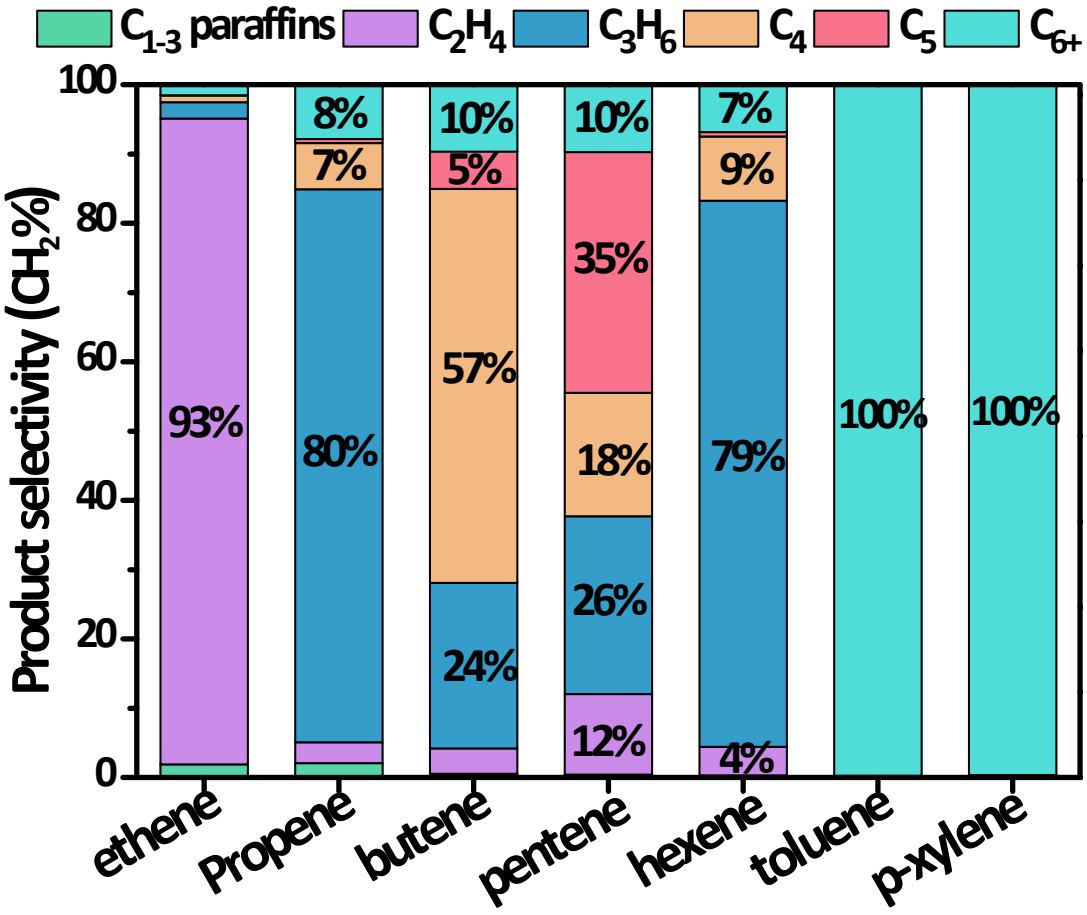

Figure S10. Product selectivity for C_{2-6} olefins, toluene, and p-xylene reaction alone over H-Beta after 65 min on stream at 450 ^{o}C. The feeding rate was equivalent to 3% of methanol (WHSV=2.0 h^{-1}) based on carbon.