Supporting information for

'Verifying the olefin formation mechanism of the methanol-to-hydrocarbons reaction over H-ZSM-48'

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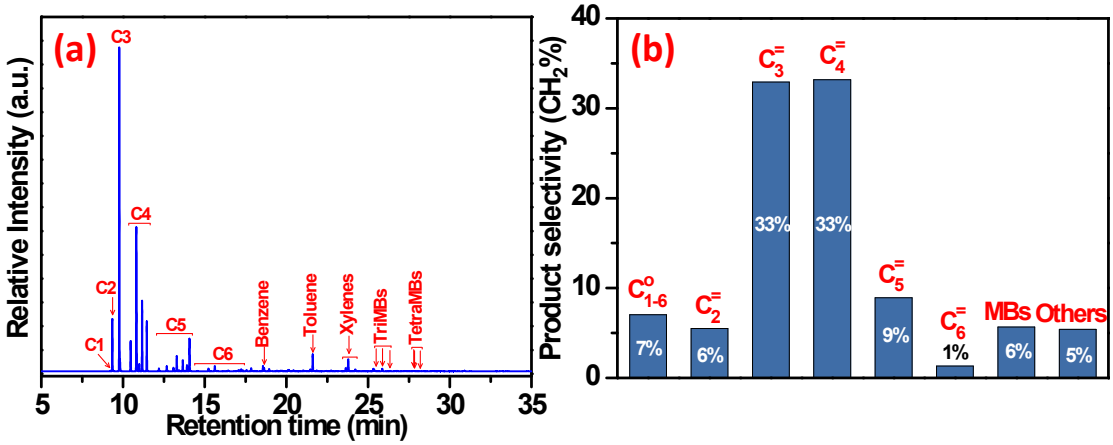

Fig. S1 GC chromatogram (a) and Product selectivity (b) of the reaction of pure tert-Butanol on zeolite H-ZSM-48. Reaction conditions: 450 °C, catalyst weight of 60 mg, tert-Butanol WHSV of 0.4 h^{-1}, TOS of 10 min.

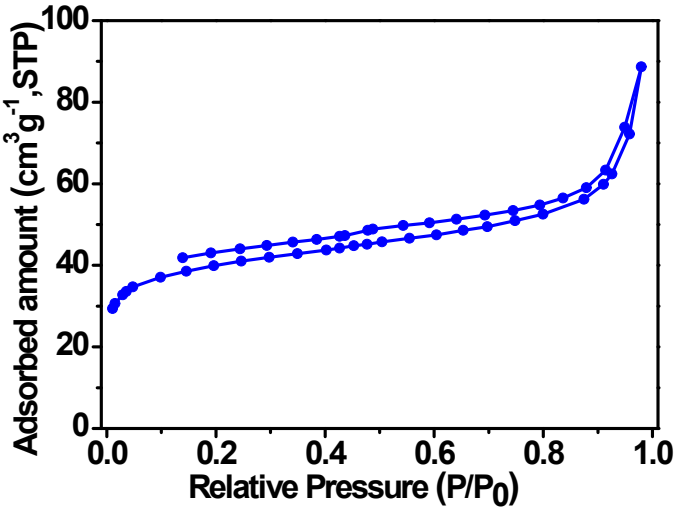

Fig. S2 N_2 adsorption-desorption isotherm of H-ZSM-48

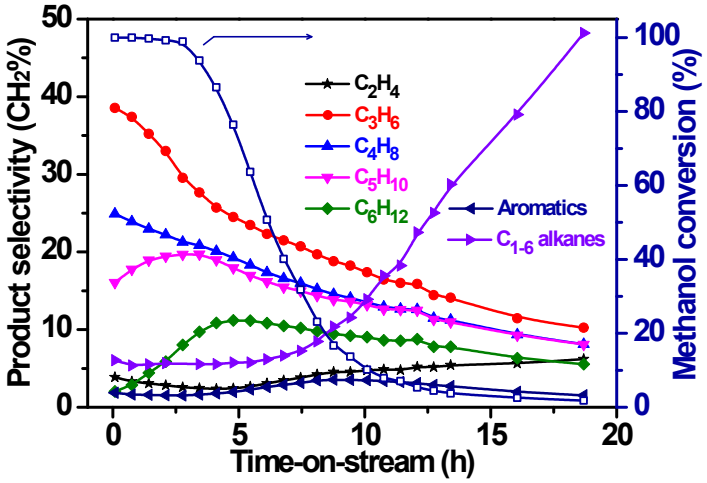

Fig. S3 Methanol conversion and product selectivity over H-ZSM-48. Reaction conditions: 17 kPa MeOH, catalyst weight of 100 mg, WHSV of 2 h^{-1} and 723 K.

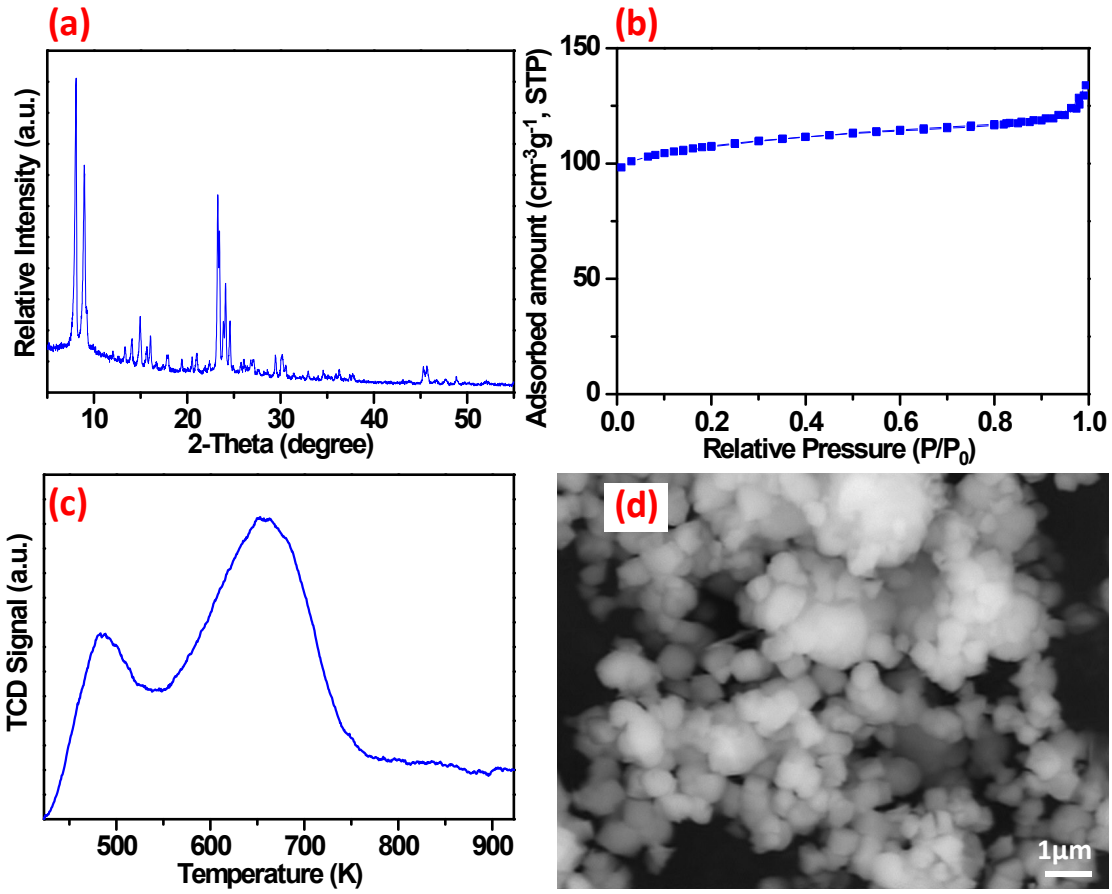

Fig. S4 XRD pattern (a), N_2 adsorption-desorption isotherm (b), NH_3-TPD profile (c), and SEM image of H-ZSM-5.

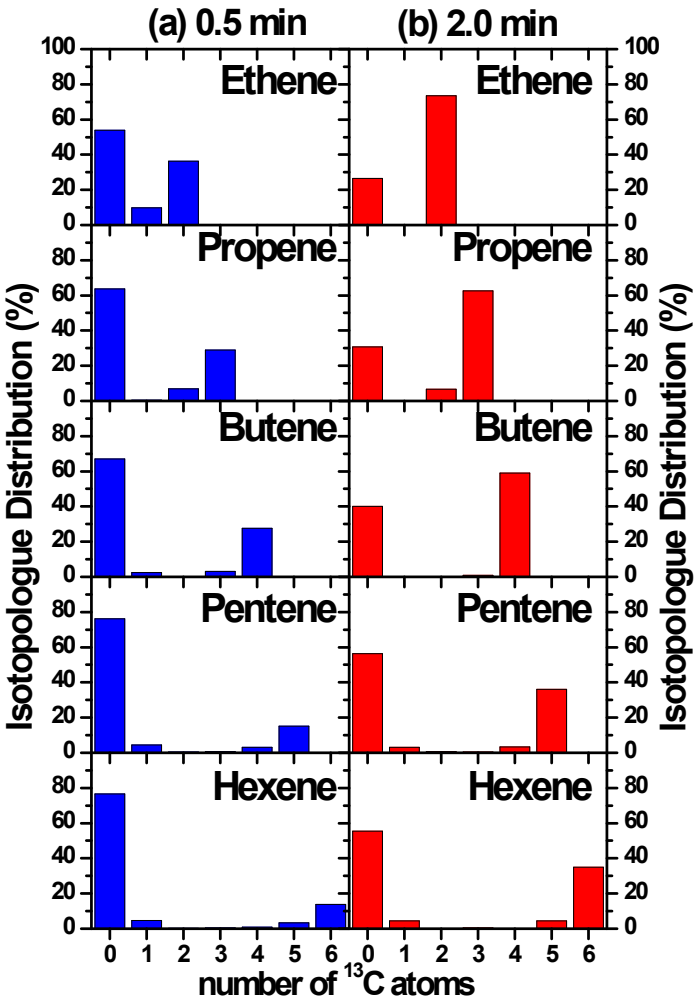

Fig. S5 Isotopic labelling patterns for effluent products formed after the $^{12}C/^{13}C$ switch experiment over H-Z-SM-48 at 723K with ^{12}C-methanol feeding for 18 min followed by 0.5 and 2 min of ^{13}C-methanol feeding and a WHSV of 25 h^{-1}.

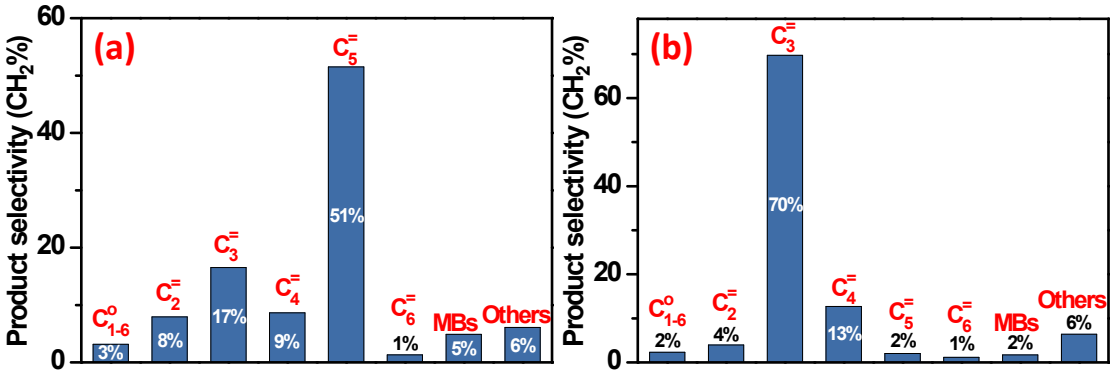

Fig. S6 Product selectivity of pentene (a) and hexene (b) alone reacted over H-ZSM-48 zeolite after 10 min on stream. Reaction conditions: 723 K, The feeding rate was equivalent to 3 C% of methanol (WHSV = 2.0 h^{-1}, Section 3.2), 1-Pentanol and 1-Hexanol were used as the precursor of pentene and hexene, respectively.

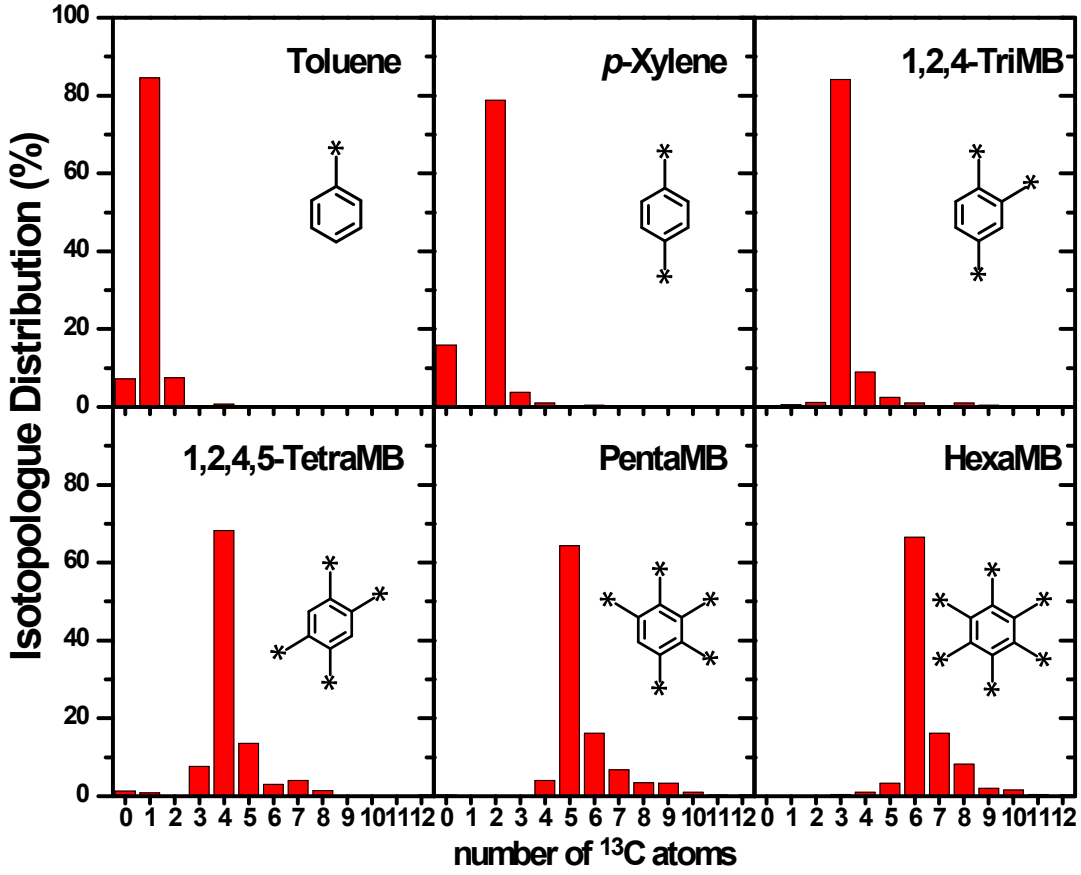

Fig. S7 Isotopic labelling patterns for methylbenzenes formed after 2 minutes of co-reacting ^{13}C methanol with ^{12}C benzene (molar ratio 3:1) at 543 K over H-ZSM-48.

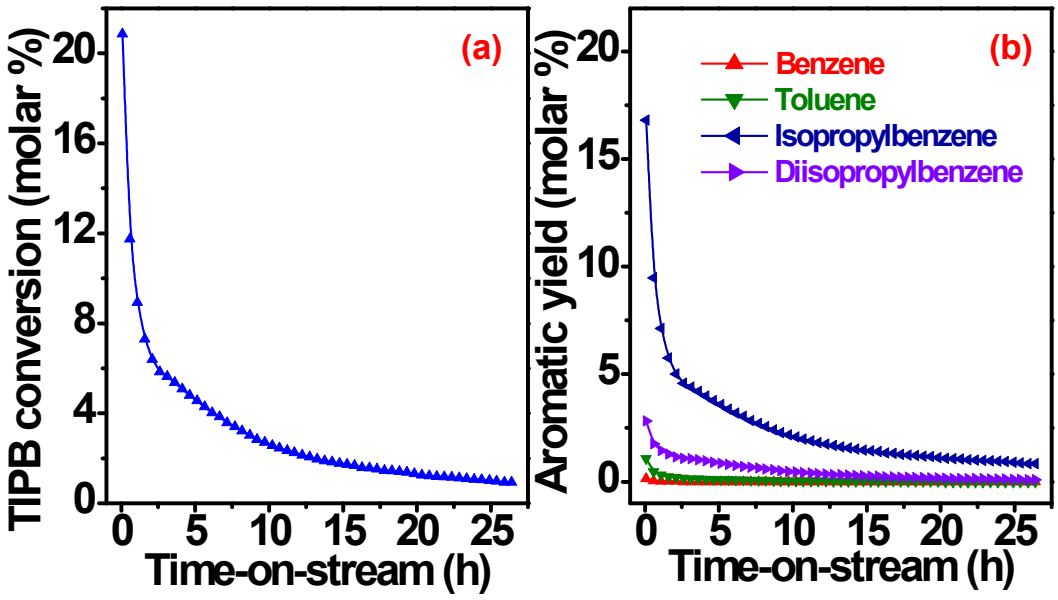

Fig. S8 TIPB conversion (a) and product distributions (b) over H-ZSM-48. Reaction conditions: 573 K, catalyst weight of 60 mg, vaporized TIPB in nitrogen (80 mL min^{-1}, 358 K) as feed.

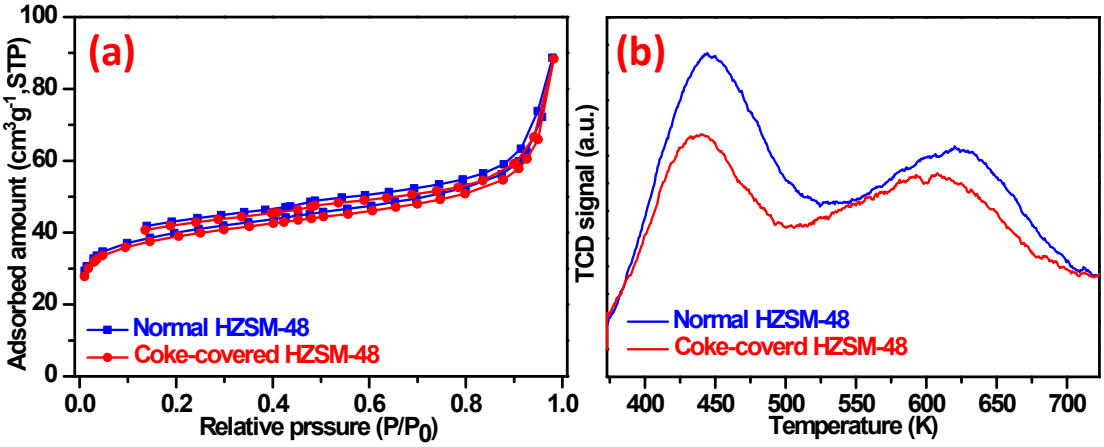

Fig. S9 Nitrogen adsorption-desorption isotherms (a) and NH_3-TPD profiles over Normal H-ZSM-48 and coke-covered H-ZSM-48.

Table S1 Methanol conversion and product selectivity over H-ZSM-48 at different reaction temperature.[a]

Temperature/K	723	823	873	973
MeOH Conversion/%	99.95	99.96	99.95	99.97
$C_{3-6}^{=}$	80.7	59.8	51.6	16.0
C_{1-6} alkanes	6.0	6.9	11.5	23.1
MBs	1.8	10.5	13.7	18.8
Product selectivity/wt% [b]				
H_2	0.00	0.00	0.01	0.00
CO	0.67	1.01	3.12	26.81
CO_2	0.31	0.30	0.89	1.53
CH_4	0.71	2.97	8.97	21.96
C_{2-6} alkanes	5.27	3.95	2.52	1.14
C_2H_4	3.84	19.85	16.40	11.51
C_3H_6	38.19	42.70	34.77	10.91
$C_4^{=}$	24.66	15.54	14.23	3.63
$C_5^{=}$	15.90	0.91	0.89	0.17
$C_6^{=}$	2.02	0.65	1.68	1.32
Benzene	0.07	1.44	1.90	5.90
Toluene	0.41	4.22	5.20	6.85
Xylene	0.98	3.97	5.17	4.67
TriMB	0.32	0.77	1.20	1.14
TetraMB	0.07	0.10	0.27	0.23
Others [c]	6.59	1.62	2.81	2.23

[a] Reaction conditions: 17 kPa MeOH, catalyst weight of 100 mg, WHSV of 2 h^{-1} and TOS of 5 min. [b] The product selectivity was analysed by a gas chromatograph (Agilent 7890A, equipped with a capillary CP-Sil PONA column and a Porapak Q packed column) with a FID detector and a TCD detector. The yields of hydrocarbon were determined with CP-Sil PONA column and FID. And, the yields of CO, CO_2, CH_4, and H_2 were determined with Porapak Q (1/8 in. × 4 m) column and TCD. He was used as carrier gas. This Agilent 7890A was configured with a ten-way valve. [c] Other fraction includes C_{7+} hydrocarbons except methylbenzenes.

Table S2 Textural and acidic properties of H-ZSM-5.

Si/Al	Surface area (m^2g^{-1})			Pore volume (cm^3g^{-1})		T_{peak} (^oC)		Acid amount [e] ($\mu mol\ g^{-1}$)		
	S_{BET} [a]	S_{micro} [b]	$S_{external}$ [b]	V_{micro} [b]	V_{meso} [c]	LT peak [d]	HT peak [d]	Total acidity	Weak acidity	Strong acidity
93.3	346	278	68	0.136	0.062	175.7	374.4	241.0	122.4	118.6

[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. [d] The LT peak represents a low temperature desorption peak. The HT peak represents a high temperature desorption peak. [e] Calculated with Gaussian function fit.

Table S3 Methanol conversion and product selectivity over H-ZSM-5 at different reaction temperature.[a]

Temperature/K	723	823	873	973
Conversion/%	100	100	100	100
C_3H_6/C_2H_4	4.3	2.4	1.8	0.7
C_4 HTI	0.13	0.06	0.04	0.04
C_5 HTI	0.27	0.34	0.29	0.41
C_6 HTI	0.61	0.42	0.16	0.02
Ethene/2MBu	3.2	25.5	79.2	331.9
$C_{3-6}^=$	69.5	63.0	50.3	14.7
C_{1-6} alkanes	10.3	7.1	9.8	32.8
Aromatics	5.4	9.3	16.8	31.2
Product selectivity/CH_2%				
CH_4	0.6	3.2	7.4	31.6
C_{2-6} alkanes	9.7	3.9	2.4	1.2
C_2H_4	9.4	19.2	21.8	17.8
C_3H_6	39.9	45.5	38.2	12.6
$C_4^=$	22.9	15.7	10.9	1.6
$C_5^=$	5.4	1.2	0.6	0.1
$C_6^=$	1.3	0.7	0.6	0.4
Benzene	0.3	0.9	2.0	7.1
Toluene	1.5	3.2	6.0	11.4
Xylene	2.8	4.0	6.9	9.4
TriMB	0.8	1.0	1.8	3.1
TetraMB	0.1	0.1	0.1	0.3
Others [b]	5.4	1.5	1.2	3.4

[a] Reaction conditions: 17 kPa MeOH, catalyst weight of 100 mg, WHSV of 2 h^{-1} and TOS of 5 min.

[b] Other fraction includes C_{7+} hydrocarbons except methylbenzenes.

Table S4 Methanol conversion and product selectivity after 18 min of the ^{12}C-methanol reaction followed by 2 min of ^{13}C-methanol reaction over H-ZSM-48 at 723 K and 44.5 kPa MeOH.

Catalyst	H-ZSM-48
WHSV/h^{-1}	25
Methanol conversion/%	62.8
C_3H_6/C_2H_4	11.3
C_4 HTI	0.01
C_5 HTI	0.06
C_6 HTI	0.21
Ethene/2MBu	0.41
Product selectivity/CH_2%	
C_{1-6} alkanes	6.5
C_2H_4	2.1
C_3H_6	23.4
$C_4^=$	19.1
$C_5^=$	18.8
$C_6^=$	11.8
Others [a]	17.1
Methylbenzenes	1.4

[a] Other fraction includes C_{7+} hydrocarbons except methylbenzenes (MBs).

Table S5 Conversion and product selectivity after 2 minutes of co-reacting ^{13}C methanol with ^{12}C benzene (molar ratio 3:1) at 543 K over H-ZSM-48.

Reaction temperature	543 K
Combined conversion of MeOH and Benzene(C%)	1.82
C_{1-6} aliphatic products (C%)	5.37
Product selectivity (C%)	
CH_4	0.22
C_2H_4	0.98
C_2H_6	0.03
C_3H_6	1.42
C_3H_8	0.03
$C_4^=$	0.52
C_4^o	0.35
$C_5^=$	0.34
C_5^o	0.79
$C_6^=$	0.00
C_6^o	0.68
Other [a]	7.32
Toluene	83.75
Xylenes	3.36
TriMBs	0.20
TetraMBs	0.00
Total	100.00

[a] Other fraction includes C_{7+} hydrocarbons except MBs.