Electronic supplementary information (ESI)

Methanol to olefins over H-RUB-13 zeolite: Regulation of framework aluminum sitting and acid density and their relation to the catalytic performance

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As the Electronic supplementary information (ESI) of the manuscript "*Methanol to olefins over H-RUB-13 zeolite: Regulation of framework aluminum sitting and acid density and their relation to the catalytic performance*", following materials are provided:

XRD patterns, SEM images, Py-IR spectra and FT-IR spectra of the H-Al-B-RUB-13 zeolites; deconvolution of the ^{27}Al MAS NMR spectra; catalytic performance of the aluminum-free H-B-RUB-13 zeolite in MTO; detailed reaction results for MTO over the H-Al-B-RUB-13 zeolites.

Table S1. Calculated absolute chemical shielding tensors (δ_{abs}) and relative chemical shifts (δ_{rel}) for the MAS NMR of ^{27}Al located at different T sites in the framework of H-RUB-13 zeolites

T site	δ_{abs} (ppm)	δ_{rel} (ppm)[a]
T1	530.1	56.8
T2	531.2	55.7
T3	529.1	57.8
T4	528.5	58.4

Note: The relative chemical shift of ^{27}Al MAS NMR is the difference between the calculated chemical shift of $Al(H_2O)_6^{3+}$ (586.9 ppm) and the absolute chemical shielding tensors of different T sites, that is, $\delta_{rel} = 586.9 - \delta_{abs}$.

Table S2. ^{27}Al chemical shifts in the isotropic protection (δ_{F1}, ppm) and in the observed dimension (δ_{F2}, ppm) as well as the isotropic chemical shifts (δ_{iso}, ppm) and the second-order quadrupolar effect parameter (S_Q, MHz) for the H-Al-B-RUB-13-170-*n* series zeolites (Si/Al ≈ 170) with different Si/B (*n*) ratios

Si/B = 47				Si/B = 85				Si/B = 155				Si/B = 239			
δ_{F1}	δ_{F2}	δ_{iso}	S_Q	δ_{F1}	δ_{F2}	δ_{iso}	S_Q	δ_{F1}	δ_{F2}	δ_{iso}	S_Q	δ_{F1}	δ_{F2}	δ_{iso}	S_Q
57.5	56.5	57.1	6.6	57.5	56.5	57.1	6.6	57.5	56.5	57.1	6.6	57.0	56.0	56.6	6.5
59.0	58.0	58.6	6.6	59.0	58.0	58.6	6.6	59.5	58.2	59.0	6.7	59.0	57.5	58.4	6.6
62.0	60.5	61.4	6.8	61.5	60.5	61.1	6.8	61.5	60.5	61.1	6.9	61.5	60.0	61.0	6.8

Note: The second-order quadrupolar effect parameter (S_Q) and isotropic chemical shifts (δ_{iso}) are obtained by: $S_Q^2 = \delta_{iso} - \delta_{F2} \times k$, $\delta_{iso} = (17\delta_{F1} + 10\delta_{F2}) / 27$, and $k = [4I \times (I + 1) - 3] / [4I \times (2I - 1) \times \nu_0]^2 \times 3 \times 105$, where I (5/2) is the spin quantum number of ^{27}Al and ν_0 is Larmor frequency.

Table S3. Chemical composition and catalytic performance of the aluminum-free H-B-RUB-13 zeolite in MTO

Item	Value
Si/B molar ratio measured by ICP-OES	15
Acidity determined by NH_3-TPD (μmol g^{-1})	10.0
Methanol conversion at 27 min on stream (%)	3.8
Selectivity to CH_4; $C_{2-4}^{=}$; and others (%)	22.5; 72.6; and 4.9
Methanol conversion at 159 min on stream (%)	1.3
Selectivity to CH_4; $C_{2-4}^{=}$; and others (%)	26.8; 68.2; and 5.0

Note: Reaction was carried out at 450 °C and atmospheric pressure, with a methanol WHSV of 1.0 h^{-1} and a carrier gas (N_2) flow of 54 mL min^{-1}. $C_{2-4}^{=}$ represents olefins from ethene to butenes.

Table S4. Reaction results of MTO over the H-Al-B-RUB-13-*m*-*n* zeolites with different Si/Al (*m*) and Si/B (*n*) ratios

H-Al-B-RUB-13-*m*-*n*	Conv. (%)	Product selectivity (%)								$C_{2-5}^{=}/C_{2-5}$
		C_1	$C_2^{=}$	$C_3^{=}$	$C_4^{=}$	$C_5^{=}$	C_{2-5}	C_{6+}	$C_{2-5}^{=}$	
H-Al-B-RUB-13-170-47	98.9	0.4	19.7	48.6	22.2	5.7	2.2	0.8	96.2	43.7
H-Al-B-RUB-13-170-85	98.4	0.5	19.1	47.9	22.6	6.1	2.6	1.0	95.7	36.8
H-Al-B-RUB-13-170-155	98.5	0.4	19.9	47.9	22.6	5.4	2.3	1.0	95.8	41.6
H-Al-B-RUB-13-170-239	98.4	0.4	19.5	47.1	22.4	5.8	3.4	1.1	94.8	27.9
H-Al-B-RUB-13-59-17	100	0.7	14.2	32.6	28.2	10.0	8.4	5.9	85.0	10.1
H-Al-B-RUB-13-76-17	100	0.6	16.6	39.5	23.9	8.8	9.1	5.8	88.8	9.6
H-Al-B-RUB-13-169-17	97.1	0.7	19.4	49.1	21.7	5.3	2.6	0.9	95.7	36.8
H-Al-B-RUB-13-276-17	90.1	0.6	19.6	47.1	24.1	6.2	1.7	0.7	97.0	57.1

Note: The MTO reactions were carried out at 400 °C and atmospheric pressure, with a methanol WHSV of 1.0 h^{-1}; the data were reported at 90 min on stream.

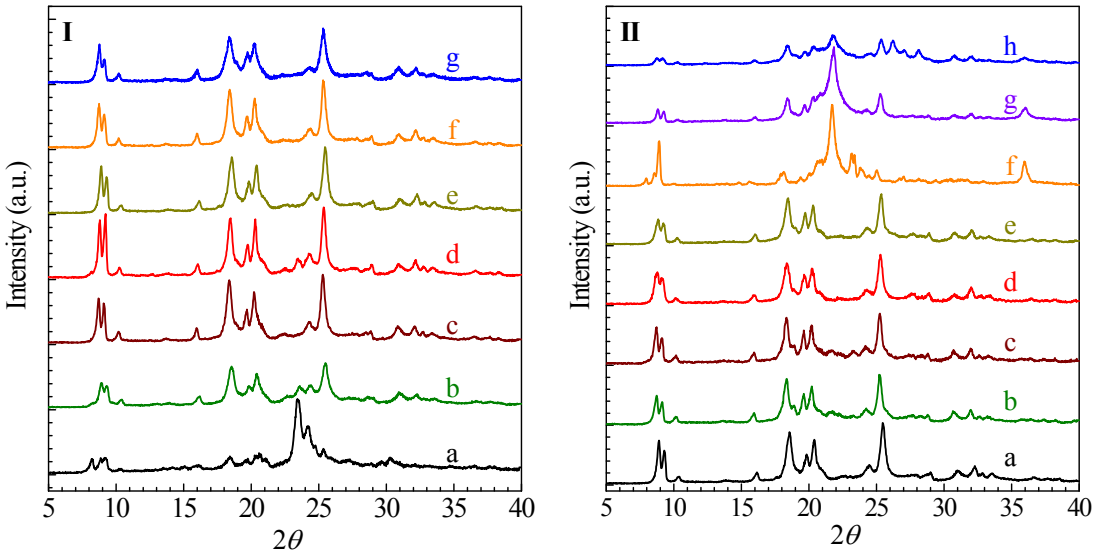

Fig. S1. XRD patterns of the as-synthesized Al-B-RUB-13 zeolites. **(I)** Prepared with Si/B = 1 and different Si/Al ratios in the synthesis gel: (a) Si/Al = 30; (b) Si/Al = 50; (c) Si/Al = 70; (d) Si/Al = 100; (e) Si/Al = 200; (f) Si/Al = 300; (g) Si/Al = ∞. **(II)** Prepared with Si/Al = 200 and different Si/B ratios in the synthesis gel: (a) Si/B = 1; (b) Si/B = 30; (c) Si/B = 70; (d) Si/B = 100; (e) Si/B = 200; (f) Si/B = 250; (g) Si/B = 300; (h) Si/B = ∞.

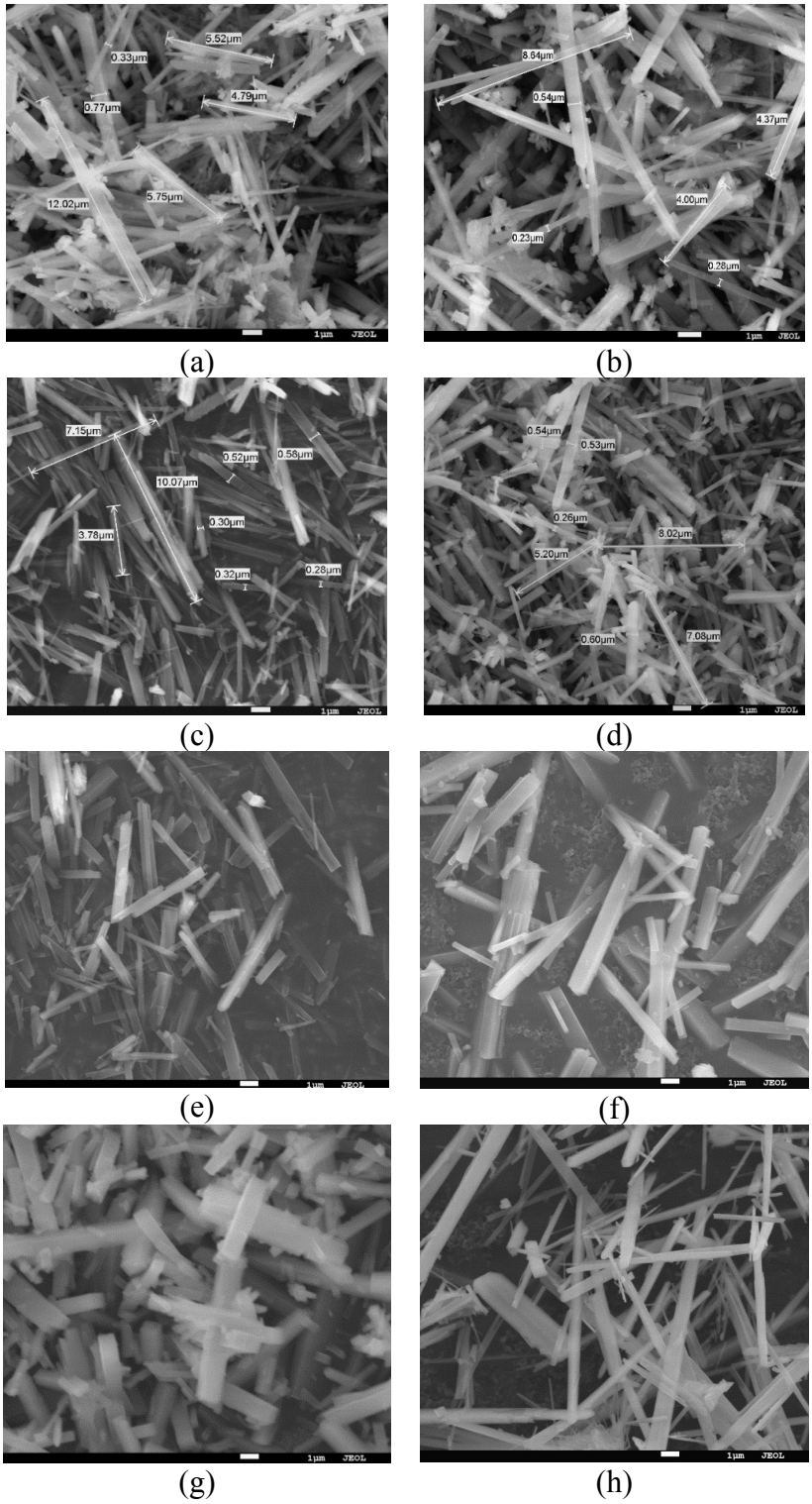

Fig. S2. SEM images of the as-synthesized Al-B-RUB-13 zeolites prepared with Si/Al = 200 and different Si/B ratios in the synthesis gel: (a) Si/B = 30; (b) Si/B = 70; (c) Si/B = 100; (d) Si/B = 200 and those prepared with Si/B = 1 and different Si/Al ratios in the synthesis gel: (e) Si/Al = 70; (f) Si/Al = 100; (g) Si/Al = 200; (h) Si/Al = 300.

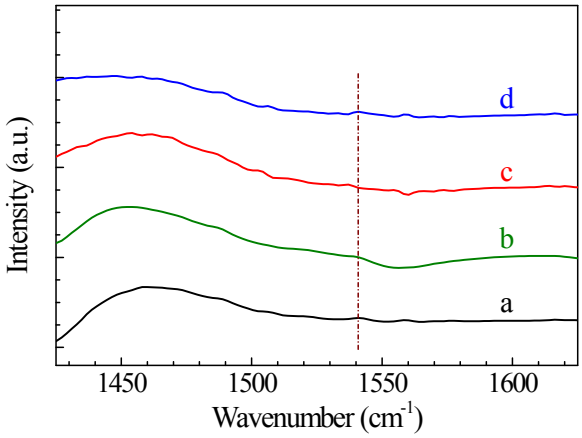

Fig. S3. Py-IR spectra collected at 150 °C for the H-Al-B-RUB-13-170-*n* series zeolites with Si/Al ≈ 170 and different Si/B (*n*) ratios: (a) Si/B = 47; (b) Si/B = 85; (c) Si/B = 155; (d) Si/B = 239.

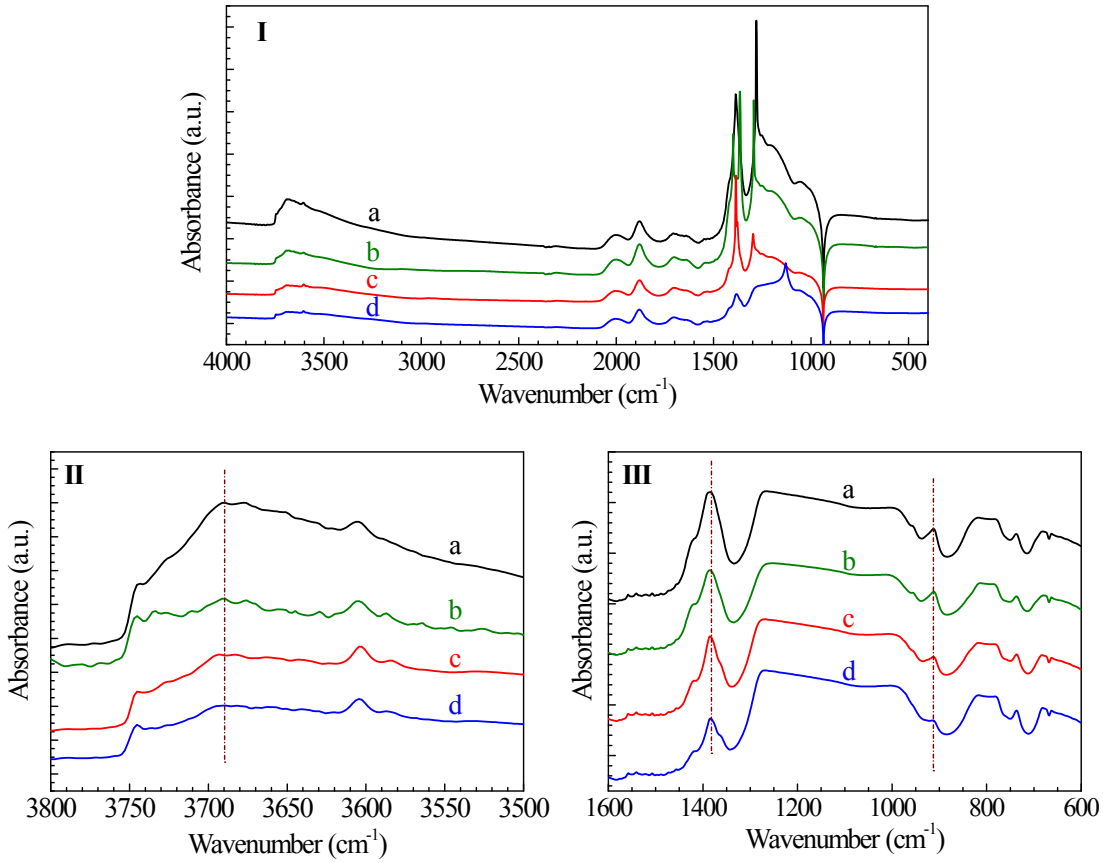

Fig. S4. FT-IR spectra in full range **(I)**, in the OH stretching vibration range **(II)**, and in the framework region **(III)** collected for the H-Al-B-RUB-13-170-*n* series zeolites with Si/Al ≈ 170 and different Si/B (*n*) ratios: (a) Si/B = 47; (b) Si/B = 85; (c) Si/B = 155; (d) Si/B = 239.

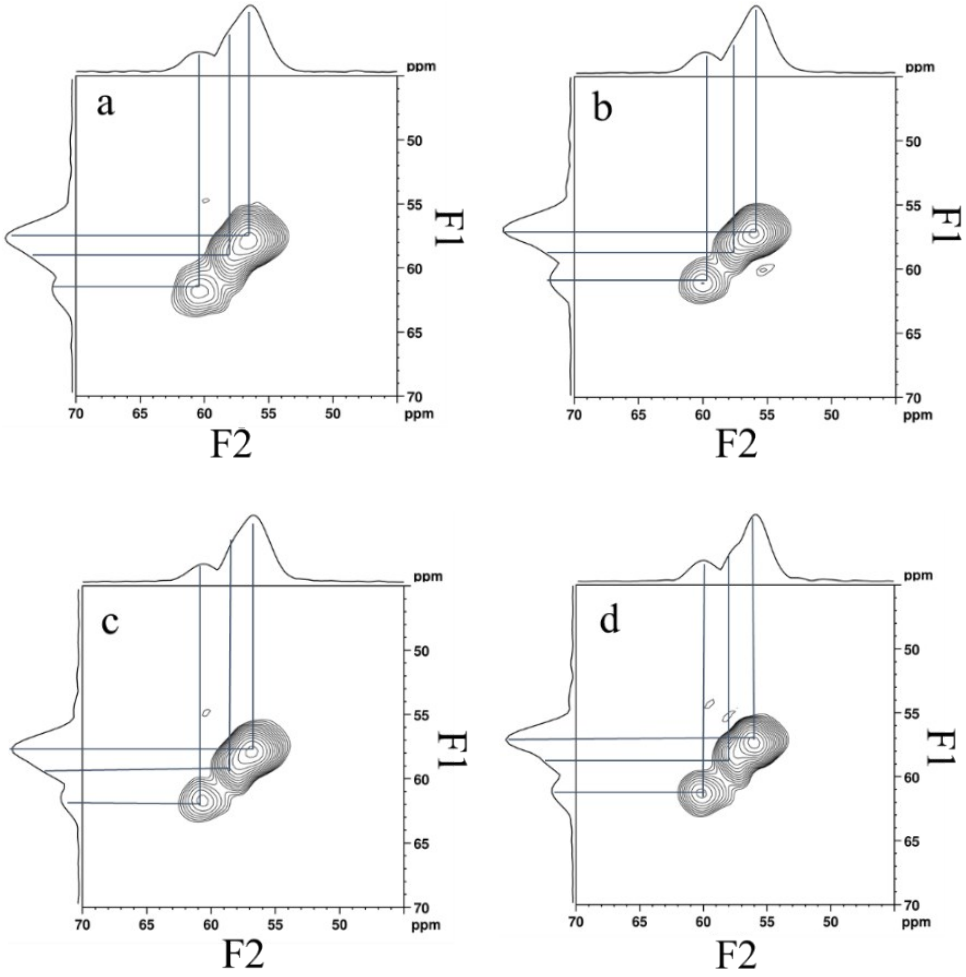

Fig. S5. 2D ^{27}Al MQ/MAS NMR spectra of the H-Al-B-RUB-13-170-*n* series zeolites with Si/Al ≈ 170 and different Si/B (*n*) ratios: (a) Si/B = 47; (b) Si/B = 85; (c) Si/B = 155; (d) Si/B = 239.

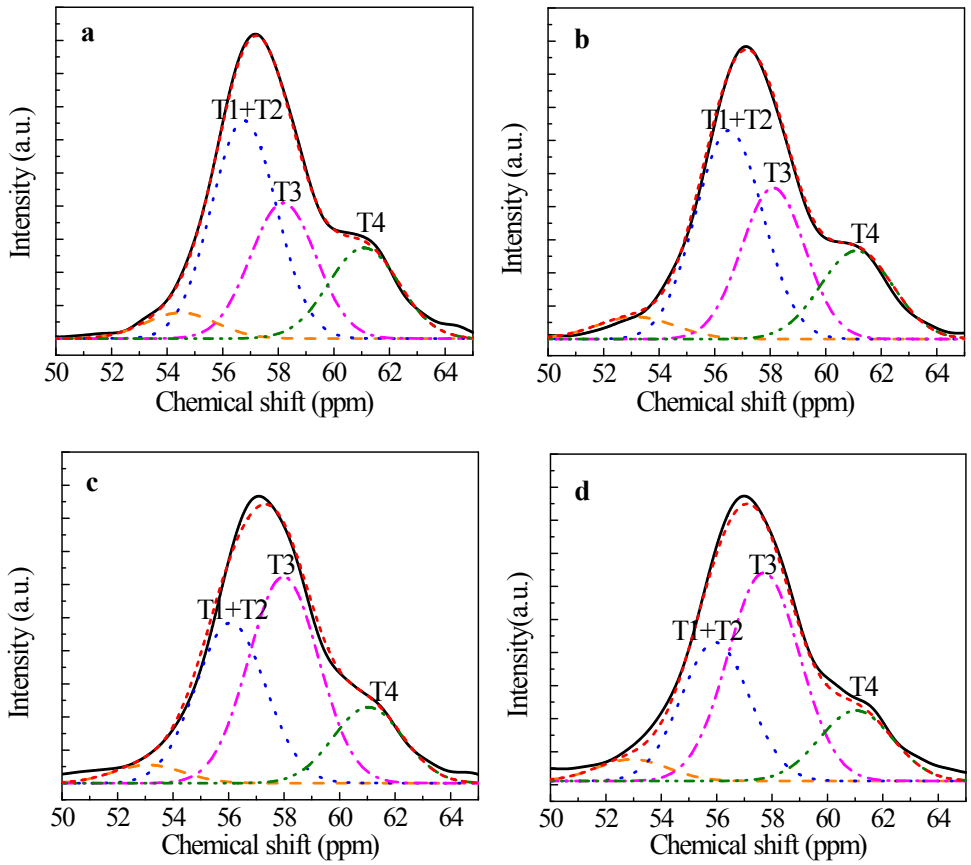

Fig. S6. Deconvolution of the ^{27}Al MAS NMR spectra of the H-Al-B-RUB-13-170-*n* series zeolites with Si/Al ≈ 170 and different Si/B (*n*) ratios: (a) Si/B = 47; (b) Si/B = 85; (c) Si/B = 155; (d) Si/B = 239. The black and red lines represent the measured and fitted curves, respectively.

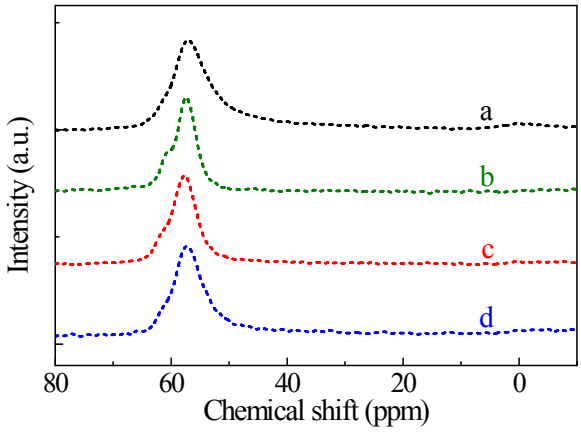

Fig. S7. ^{27}Al MAS NMR spectra of the H-Al-B-RUB-13-*m*-17 seires zeolites with Si/B ≈ 17 and different Si/Al (*m*) ratios: (a) Si/Al = 59; (b) Si/Al = 76; (c) Si/Al = 169; (d) Si/Al = 276.

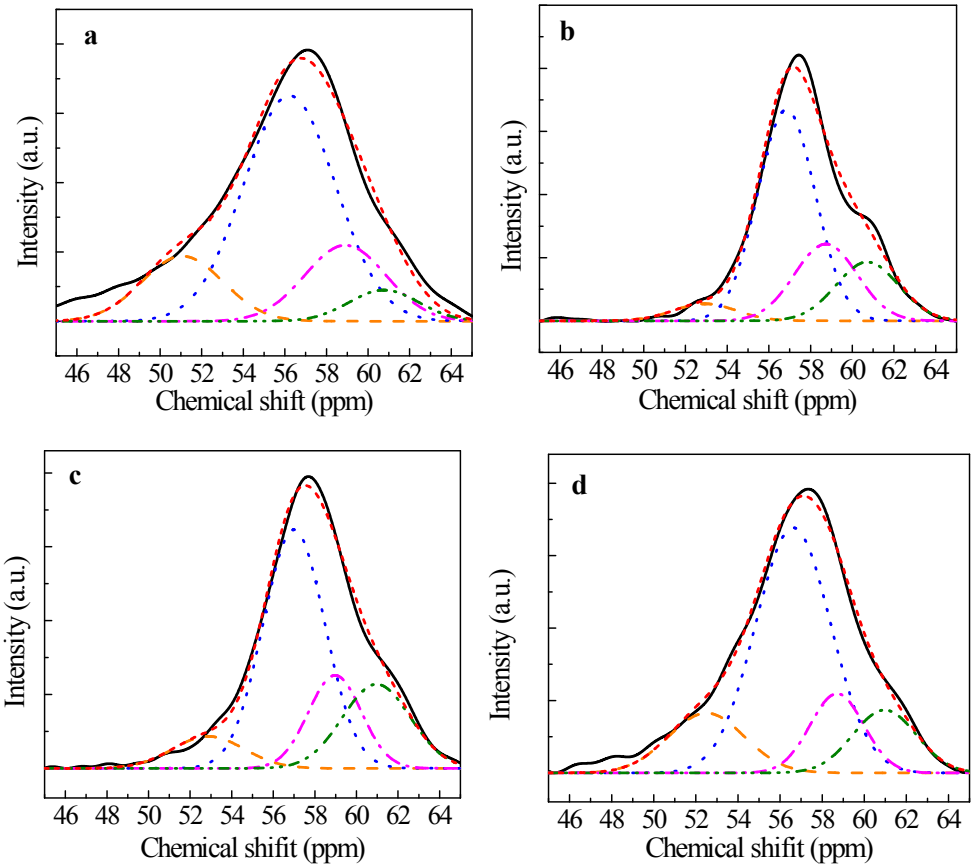

Fig. S8. Deconvolution of the ^{27}Al MAS NMR spectra of the H-Al-B-RUB-13-*m*-17 seires zeolites with Si/B ≈ 17 and different Si/Al (*m*) ratios: (a) Si/Al = 59; (b) Si/Al = 76; (c) Si/Al = 169; (d) Si/Al = 276. The black and red lines represent the measured and fitted curves, respectively.

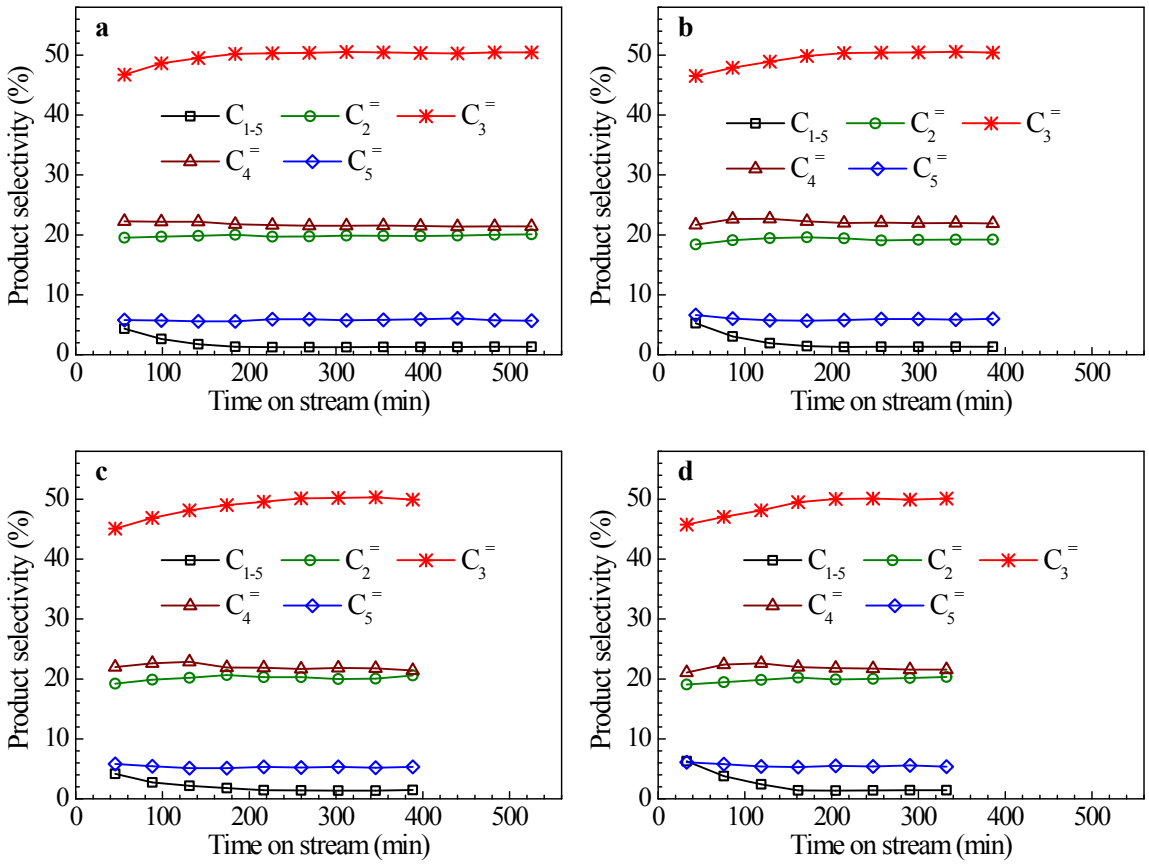

Fig. S9. Products distribution profiles for MTO over H-Al-B-RUB-13-170-*n* series zeolites with Si/Al ≈ 170 and different Si/B (*n*) ratios: (a) Si/B = 47; (b) Si/B = 85; (c) Si/B = 155; (d) Si/B = 239. The reactions were carried out in a fixed-bed reactor at 400 °C and atmospheric pressure, with a methanol WHSV of 1.0 h^{-1}.

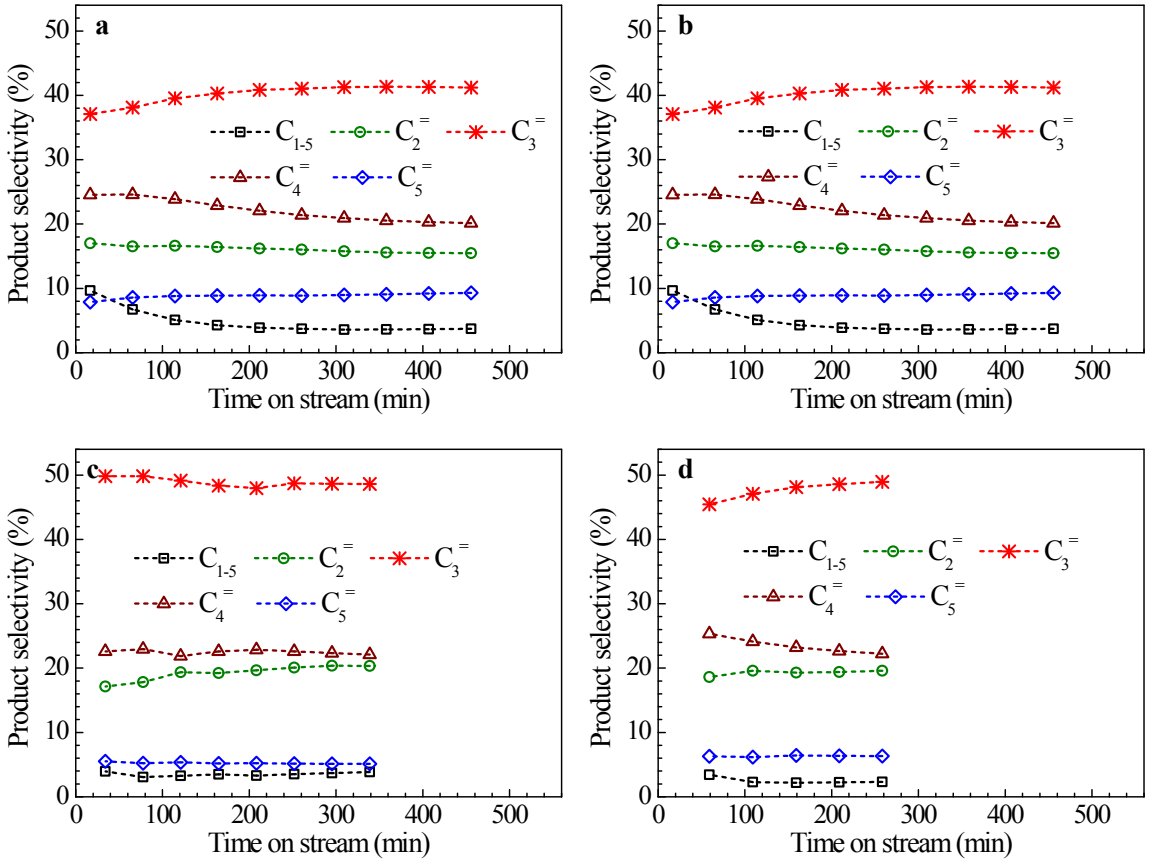

Fig. S10. Products distribution profiles for MTO over H-Al-B-RUB-13-*m*-17 series zeolites with Si/B ≈ 17 and different Si/Al (*m*) ratios: (a) Si/Al = 59; (b) Si/Al = 76; (c) Si/Al = 169; (d) Si/Al = 276. The reactions were carried out in a fixed-bed reactor at 400 °C and atmospheric pressure, with a methanol WHSV of 1.0 h^{-1}.

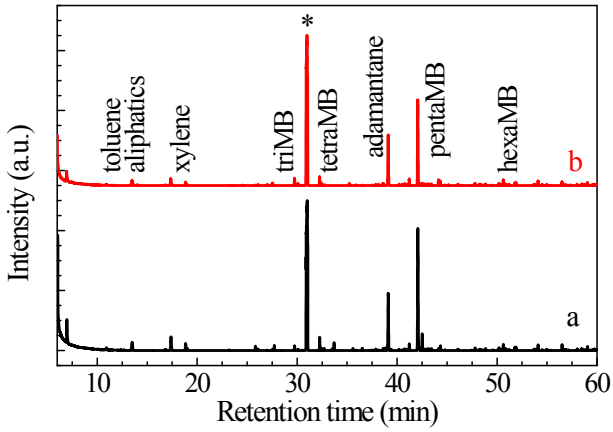

Fig. S11. GC-MS chromatograms of the organic species retained in H-Al-B-RUB-13-170-47 (a) and H-Al-B-RUB-13-170-85 after the $^{12}C/^{13}C$-methanol switch experiment at 300 °C. The symbol "*" represents the internal standard (hexachloroethane).