Supporting Information for

Understanding the Correlation between Ga Speciation and Propane Dehydrogenation Activity on Ga/H-ZSM-5 Catalysts

Yong Yuan[1], Casper Brady[1], Raul F. Lobo[1], Bingjun Xu*[1,2]

[1]Center for Catalytic Science and Technology, Department of Chemical and Biomolecular

Engineering, University of Delaware, Newark, Delaware 19716, United States

[2]College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

Email: b_xu@pku.edu.cn

Table S1. Physical and chemical properties of H-ZSM-5 samples investigated in this work.

Sample	Si/Al ratio[a]	BAS density ($\mu mol \cdot g^{-1}$)[b]	Micropore volume[c] ($cm^3 \cdot g^{-1}$)
H-ZSM-5(15)	15.4 ± 1.3	636	0.12
H-ZSM-5(28)	27.5 ± 1.9	460	0.12
H-ZSM-5(39)	39.0 ± 2.8	281	0.13

[a]Determined by XRF.
[b]Measured by pyridine adsorption FTIR.
[c]Calculated with the *t*-plot method obtained from N_2 physisorption isotherms.

Table S2. Composition properties of the prepared Ga/H-ZSM-5 samples.

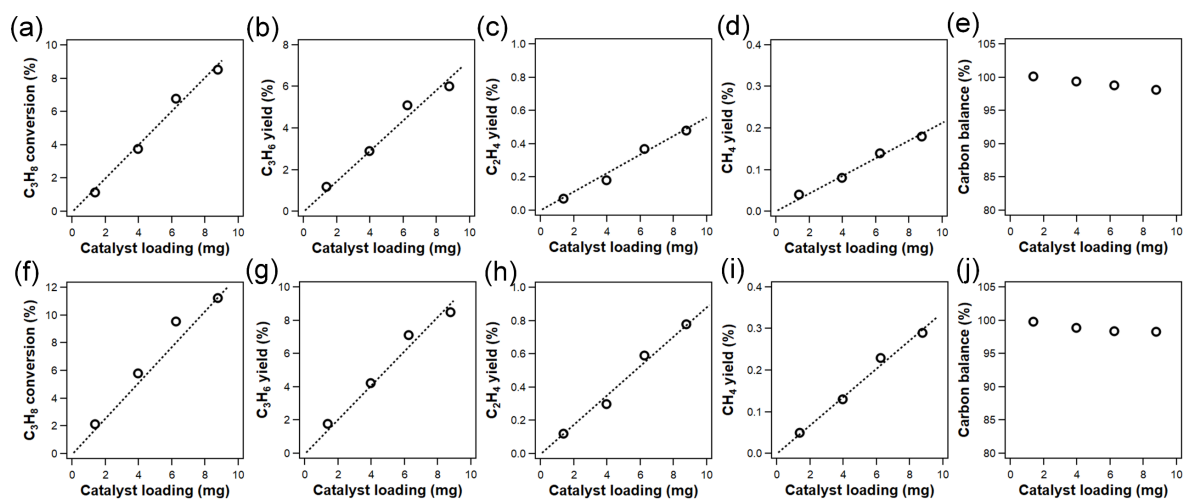| Sample	Ga/Al ratio[a]	Ga loading (%)[a]
Ga/H-ZSM-5(15)		
	0.014	0.10
	0.024	0.16
	0.042	0.28
	0.061	0.42
	0.074	0.51
	0.083	0.55
	0.13	0.89
	0.21	1.52
	0.31	2.18
	0.45	3.29
	0.56	3.75
	0.7	5.07
	1.0	6.61
	1.3	8.27
	1.7	11.60
Ga/H-ZSM-5(28)		
	0.025	0.10
	0.071	0.28
	0.097	0.37
	0.15	0.62
	0.32	1.28
	0.44	1.77
	0.52	2.05
	0.7	2.80
	1.0	4.05
	1.3	5.25
	1.7	6.88
Ga/H-ZSM-5(39)		
	0.12	0.35
	0.26	0.76
	0.44	1.24
	0.55	1.54
	0.67	1.89
	1.0	2.96
	1.3	3.68
	1.7	5.04

[a]Determined by XRF.

Figure S1. (a-e) C_3H_8 conversion, C_3H_6 yield, C_2H_4 yield, CH_4 yield and carbon balance as a function of the catalyst loading over Ga/H-ZSM-5 (Si/Al = 15 and Ga/Al =0.21) at 550 °C. (f-j) C_3H_8 conversion, C_3H_6 yield, C_2H_4 yield, CH_4 yield and carbon balance as a function of the catalyst loading over Ga/H-ZSM-5 (Si/Al = 15 and Ga/Al =0.21) at 570 °C. Reaction conditions: C_3H_8 partial pressure, 5.07 kPa with balancing N_2 (total flow rate was 100 mL·min^{-1}).
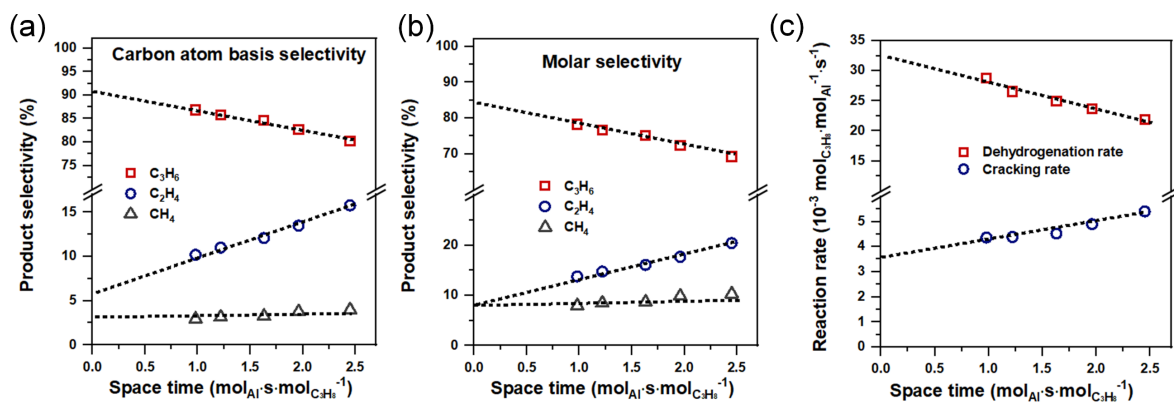
Figure S2. Product selectivity (a) on carbon atom basis and (b) on molar basis and (c) C_3H_8 dehydrogenation rates and C_3H_8 cracking rates (normalized by a per Al basis) as a function of space time over Ga/H-ZSM-5 (Si/Al = 15 and Ga/Al =0.21). Reaction conditions: 550 °C; C_3H_8 partial pressure, 5.07 kPa with balancing N_2. Dotted lines indicate linear extrapolations to zero space time.
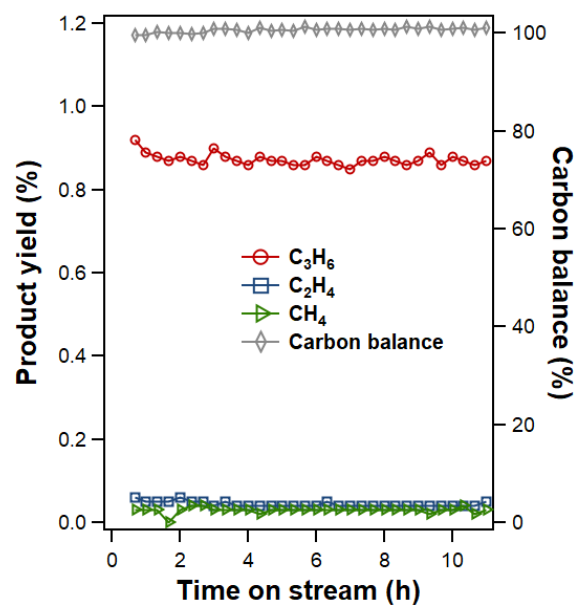
Figure S3. PDH product yield and carbon balance as a function of time on stream over Ga/H-ZSM-5 (Si/Al = 15 and Ga/Al = 1.0). Reaction conditions: 550 °C; C_3H_8 partial pressure, 5.07 kPa with balancing N_2; space time, 1.17 $mol_{Al}·s·mol_{C3H8}^{-1}$.
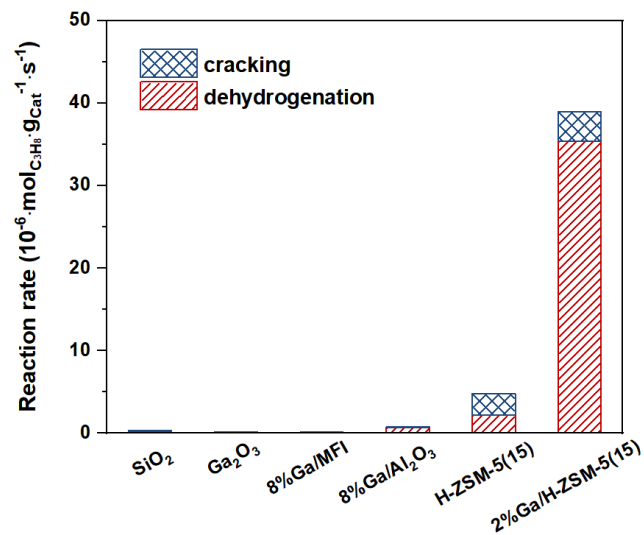
Figure S4. C_3H_8 dehydrogenation rates and cracking rates over various catalysts. Reaction conditions: 550 °C; C_3H_8 partial pressure, 5.07 kPa with balancing N_2; space time, 13440 $g_{Cat} \cdot s \cdot mol_{C3H8}^{-1}$. The propane conversions are below 5.5% in the rate measurements.
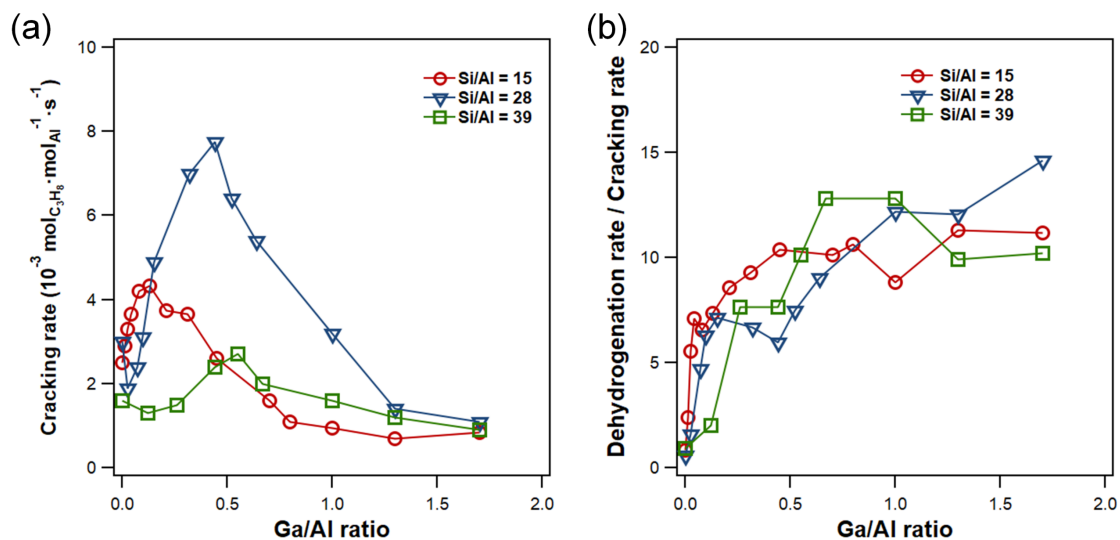
Figure S5. (a) C_3H_8 cracking rate (normalized by a per Al basis) and (b) the ratio of C_3H_8 dehydrogenation rate to C_3H_8 cracking rate as a function of Ga/Al ratio on H-ZSM-5 with three Si/Al ratios (15, 28, 39). Reaction conditions: 550 °C; C_3H_8 partial pressure, 5.07 kPa with balancing N_2.

Text S1. Simulation of PDH activation energy of exchanged Ga species based on a dual-site model

Assuming that there are two types of active sites on the Ga/H-ZSM-5 for PDH reaction at low Ga/Al ratios, i.e., BAS and exchanged Ga species, respectively. The assumption is reasonable since linear increase relationship between TOF_{Al} and Ga/Al ratio has been observed at low Ga/Al ratios (Figure 1). Thus, the TOF_{Al} can be decoupled by the contribution from remaining BAS and exchanged Ga species, as shown in eq S1:

$$TOF_{Al} = x_1 \cdot TOF_1 + x_2 \cdot TOF_2 \tag{S1}$$

where x_1 and x_2 represent the ratio of remaining BAS/Al ratio and Ga/Al ratio, respectively. TOF_1 and TOF_2 represent the TOF_{H+} (PDH rate normalized on a per BAS basis) and the TOF of exchanged Ga species, respectively. We note that $x_1 + x_2 < 1$, as the measured BAS density is lower than that of Al density in the parent zeolites employed to prepare Ga/H-ZSM-5.[1-3] The TOF of the exchanged Ga species could be determined from TOF_{Ga} (shown in Figure 1b) divided by the stoichiometry ratio between the replacement of BAS and Ga atom determined in our previous work.[1] One Ga atom roughly replaces one BAS at low Ga/Al ratio (≤ 0.5) on Si/Al ratio of 15, and one Ga atom roughly replaces 0.6 BAS at low Ga/Al ratio (≤ 0.52) on Si/Al ratio of 39.[1] TOF could be expressed as eq S2 below:

$$TOF = k \cdot P_{propane} = A \cdot e^{-Ea/RT} \cdot P_{propane} \tag{S2}$$

where k and $P_{propane}$ represent the rate constant and the partial pressure of propane, respectively. A, E_a and R represent pre-exponential factor, activation energy, and gas constant, respectively. Multiple studies have confirmed that propane is first order in the reaction.[4, 5] Thus, the TOF_{Al} can be represented as shown in eq S3:

$$TOF_{Al} = x_1 \cdot A_1 \cdot e^{-E_{a1}/RT} \cdot P_{propane} + x_2 \cdot A_2 \cdot e^{-E_{a2}/RT} \cdot P_{propane} \tag{S3}$$

where the subscripts 1 and 2 represent the BAS and exchanged Ga species (Ga^+–H^+ pair sites or isolated Ga^+ sites), respectively. We note that the H^+ in the Ga^+–H^+ pair site is still counted as a BAS capable of catalyzing the PDH in the current model. This assumption is not expected to have a significant impact on

the overall result because of the low concentration of $Ga^+–H^+$ pair sites, e.g., highest density of the $Ga^+–H^+$ pair sites in Ga/H-ZSM-5 (Si/Al = 15) occurs as a Ga/Al ratio of 0.042.[1] Based on eq S2, the apparent activation E_{app} could be derived to eqs S4 and S5:

$$E_{app} = -R \frac{d\left(\ln\left(TOF_{Al}\right)\right)}{d\left(1/T\right)} = -\frac{R}{TOF_{Al}}\left[x_1 \cdot A_1 \cdot P_{propane} \cdot e^{-E_{a1}/RT}\left(\frac{-E_{a1}}{R}\right) + x_2 \cdot A_2 \cdot P_{propane} \cdot e^{-E_{a2}/RT}\left(\frac{-E_{a2}}{R}\right)\right] \qquad (S4)$$

$$E_{app} = \frac{x_1 \cdot TOF_1 \cdot E_{a1} + x_2 \cdot TOF_2 \cdot E_{a2}}{x_1 \cdot TOF_1 + x_2 \cdot TOF_2} \qquad (S5)$$

Based on eq S5, The E_{app} of the exchanged Ga species on Si/Al ratios of 15 and 39 with Ga/Al ratio from 0 − 0.042 and 0 − 0.55 were obtained by fitting using the least square method. The fitting conditions and results are summarized as in Table S3.

Table S3. Summary of simulation conditions and results of the dual-site model.

Si/Al ratio	Ga/Al range	x_1+x_2[a]	TOF$_1$ $(mol_{C3H8} \cdot mol_H^{-1} \cdot s^{-1})$[b]	TOF$_2$ $(mol_{C3H8} \cdot mol_{Ga}^{-1} \cdot s^{-1})$[c]	Ea$_1$ $(kJ \cdot mol^{-1})$[d]	Ea$_2$ $(kJ \cdot mol^{-1})$[e]	R^2
15	0-0.042	0.612	0.00337±0.00008	0.597±0.091	188±7.9	90.8±1.5	0.997
39	0-0.55	0.694	0.00222±0.00017	0.075±0.008	156±4.1	117±2.4	0.934

[a]x_1 and x_2 represent the fraction of BAS, Ga$^+$–H$^+$ pair sites (Si/Al = 15) or isolated Ga$^+$ sites (Si/Al = 39) to the Al amount of each sample, respectively. x_1+x_2 represents the BAS/Al ratio of H-ZSM-5 with each Si/Al ratio, BAS concentration is determined on pyridine adsorption FTIR results and Al content are calculated based on Si/Al ratio determined by XRF (Table S1). The chemical stoichiometry that one Ga atom roughly replaces one BAS at low Ga/Al ratio has been applied on Si/Al ratio of 15, and that one Ga atom roughly replaces 0.6 BAS at low Ga/Al ratio has been applied on Si/Al ratio of 39.[1]

[b]TOF$_{H+}$ (PDH rate on a per BAS basis) was determined from the TOF$_{Al}$ divided by the BAS/Al ratio on H-ZSM-5 without Ga. (0.612 on Si/Al ratio of 15 and 0.694 on Si/Al ratio of 39).

[c]TOF$_{Ga+–H+}$ (Si/Al = 15) and TOF$_{Ga+}$ (Si/Al = 39) on Ga/H-ZSM-5 at low Ga/Al ratios were determined from the TOF$_{Ga}$ (showin in Figure 1b) divided by the stoichiometry ratio between the replacement of BAS and Ga atom on the reduced Ga/H-ZSM-5 determined in our previous work.[1] (1 on Si/Al ratio of 15 and 0.6 on Si/Al ratio of 39).

[d]E$_{app}$ of PDH on BAS obtained by parent H-ZSM-5 without Ga.

[e]Fitted E$_{app}$ of PDH on exchanged Ga species, which decouples the effect of remaining BAS.

A triple-site model is needed when BAS, Ga^+–H^+ pair sites and isolated Ga^+ sites are all present on a catalyst with Si/Al ratio of 28 and Ga/Al ratio at or below 0.52. The fraction of the exchanged Ga in the forms of Ga^+–H^+ pair sites and isolated Ga^+ sites to the Al amount can be determined based on eqs S6–S8:

$$TOF_{Al} = x_1 \cdot TOF_1 + x_2 \cdot TOF_2 + x_3 \cdot TOF_3 \tag{S6}$$

$$x_1 + x_2 + x_3 = BAS/Al \text{ ratio} \tag{S7}$$

$$x_2 + x_3 = Ga/Al \text{ ratio} \tag{S8}$$

where the subscripts 1, 2 and 3 represent the BAS, Ga^+–H^+ pair sites and isolated Ga^+ sites, respectively. It should be noted that TOF_1, TOF_2 and TOF_3 are known variables since they are determined via either direct measurements (TOF_1) or fitting in the dual-site model. Similar derivations as in the dual-site model lead to the following expression of the E_{app}:

$$E_{app} = \frac{x_1 \cdot TOF_1 \cdot E_{a1} + x_2 \cdot TOF_2 \cdot E_{a2} + x_3 \cdot TOF_3 \cdot E_{a3}}{x_1 \cdot TOF_1 + x_2 \cdot TOF_2 + x_3 \cdot TOF_3} \tag{S9}$$

where E_{a1}, E_{a2} and E_{a3} in the triple-site model are known variables since they are determined via either direct measurements (E_{a1}) or fitting in the dual-site model. Taking into account the experimental error for the measured activity and measured E_{app}, the fraction of three types of active sites is determined by solving eqs S6-S8 within errors of ±15% (including TOF_1, TOF_2, TOF_3, TOF_{Al}, BAS/Al ratio, Ga/Al ratio). Then, the E_{app} are calculated for Ga/H-ZSM-5 (Si/Al = 28) samples with Ga/Al ≤ 0.52 using eq S9 within errors of ±15% (including Ea_1, Ea_2, Ea_3). The results are summarized in Table S4 and plotted in Figure 4. We note that the triple-site model cannot be applied to samples that might contain a fourth type of site, e.g., Ga^+-Ga^+, thus, no attempt was made to use this model on Ga/H-ZSM-5 (Si/Al = 15) samples with Ga/Al > 0.1, and Ga/H-ZSM-5 (Si/Al = 28) samples with Ga/Al > 0.52.

Table S4. Summary of calculated fraction of different active species and E_{app} of PDH on Si/Al ratio of 28 with Ga/Al ratios ranging from 0 to 0.52.

Ga/Al ratio	x_1[a]	x_2[a]	x_3[a]	E_{app} (cal) (kJ·mol^{-1})[b]	E_{app} (exp) (kJ·mol^{-1})[c]
0	0.664–0.898	0.000	0.000	140–190	166
0.025	0.643–0.869	0.000–0.000	0.021–0.031	121–164	153
0.071	0.604–0.817	0.003–0.007	0.054–0.079	94.4–137	133
0.097	0.581–0.787	0.015–0.020	0.063–0.097	87.4–125	124
0.015	0.536–0.726	0.039–0.046	0.081–0.134	83.4–117	110
0.32	0.392–0.530	0.035–0.049	0.223–0.333	86.5–123	99.5
0.44	0.290–0.392	0.014–0.034	0.341–0.492	90.6–131	99.8
0.52	0.222–0.300	0.004–0.027	0.415–0.594	92.6–134	106

[a]x_1, x_2, and x_3 represent the fraction of BAS, Ga^+–H^+ pair sites and isolated Ga^+ sites to the Al amount of each sample. The BAS/Al ratio of H-ZSM-5 with Si/Al ratio of 28 is 0.781. BAS concentration is determined on pyridine adsorption FTIR results and Al amount are calculated based on Si/Al ratio determined by XRF. Ga/Al ratios are measured by XRF. TOF_{Al} are Al normalized PDH rates, as shown in Figure 1. TOF_1, TOF_2 and TOF_3 are 0.00232, 0.597 and 0.075 mol_{C3H8} mol_{Ga}^{-1} s^{-1}, respectively. The fitted x_1, x_2, x_3 are obtained by eqs S6-S8 within 15% error.

[b]Calculated E_{app} based on eq S9. E_{a1}, E_{a2} and E_{a3} are 166, 90.8 and 117 kJ·mol^{-1}, respectively. The calculated E_{app} are within 15% error.
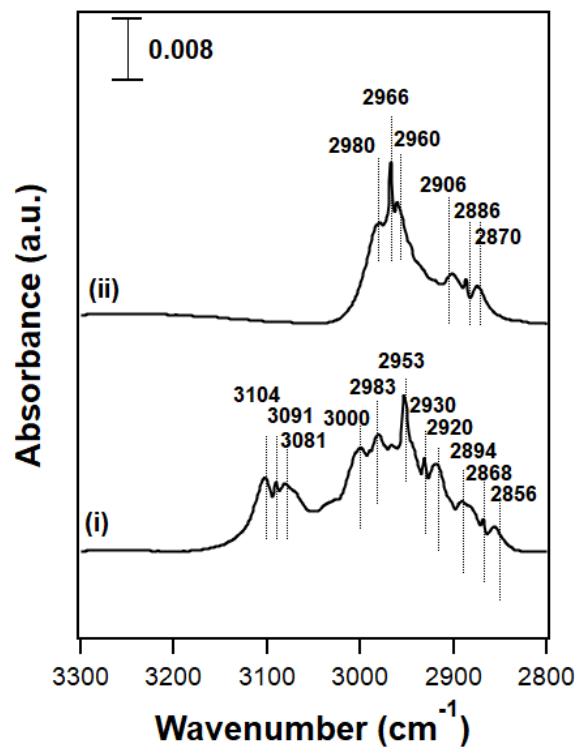
[c]Experimatal E_{app}.

Figure S6. FTIR spectra of (i) C_3H_6 with 0.27 kPa and (ii) C_3H_8 with 0.07 kPa at 25 °C. The background spectrum was collected in the spectral cell without a sample pellet at 25 °C under vacuum.
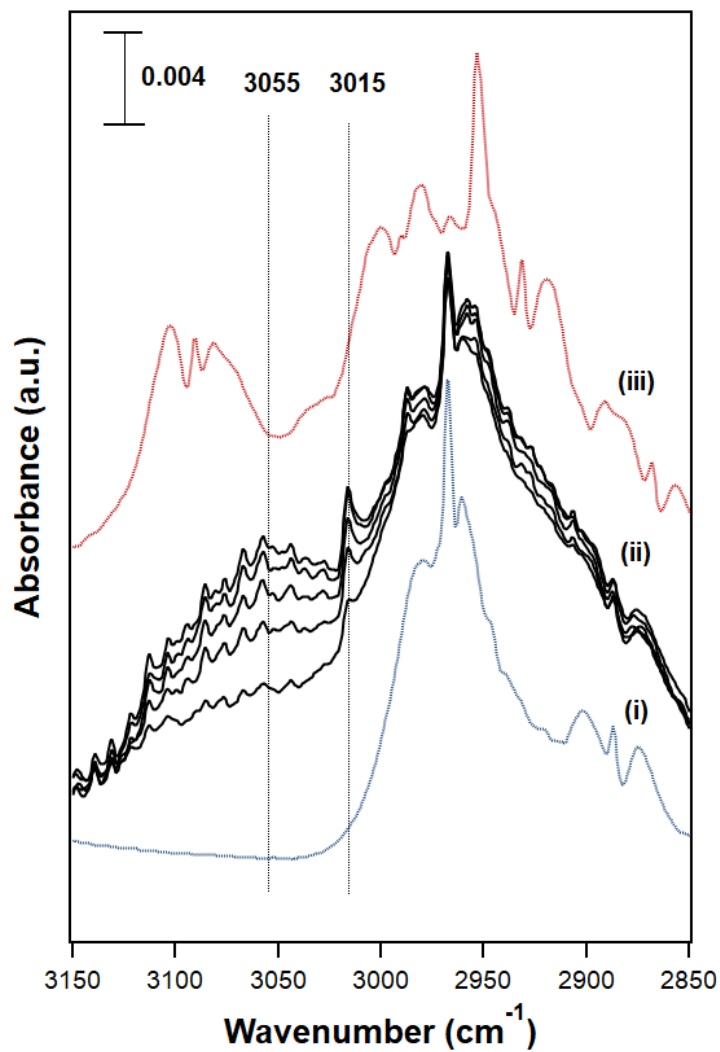
Figure S7. FTIR spectra of (i) C_3H_8 gas phase, (ii) C_3H_8 treatment on reduced Ga/H-ZSM-5 (Si/Al = 15, Ga/Al = 0.13) for 2, 4, 6, 8, and 10 min, respectively (from bottom to up, Figure 5a), and (iii) C_3H_6 gas phase. All spectra are normalized to the highest peak intensity of the C_3H_8 gas phase spectrum for clarity.
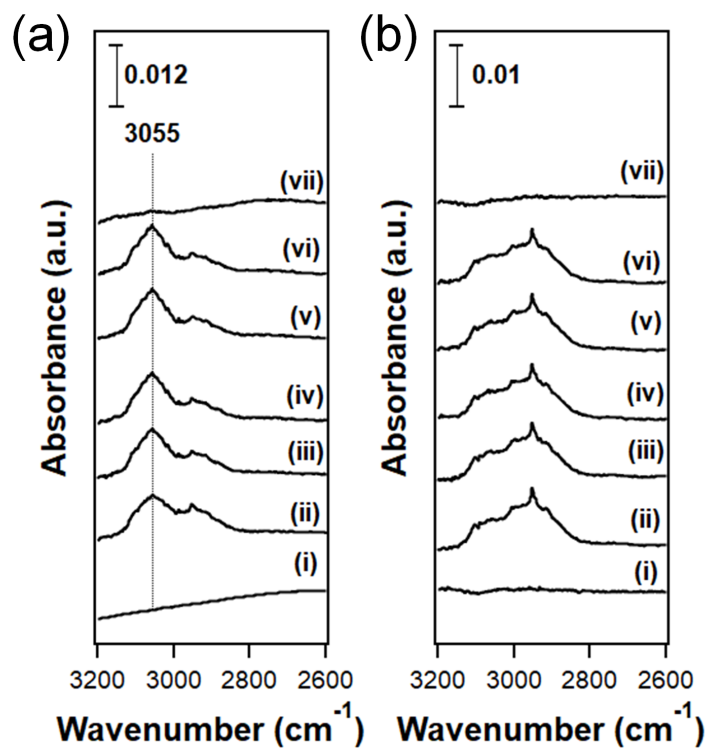
Figure S8. FTIR spectra of C_3H_6 treatment on (a) reduced Ga/H-ZSM-5 (Si/Al = 15, Ga/Al = 0.13) and (b) H-ZSM-5 (Si/Al = 15) at 550 °C: (i) before C_3H_6 treatment; (ii-vi) C_3H_6 treatment (0.27 kPa) for 2, 4, 6, 8, and 10 min, respectively; (vii) after evacuation. The background spectrum is collected in the spectral cell with a dehydrated sample pellet at 550 °C under vacuum.
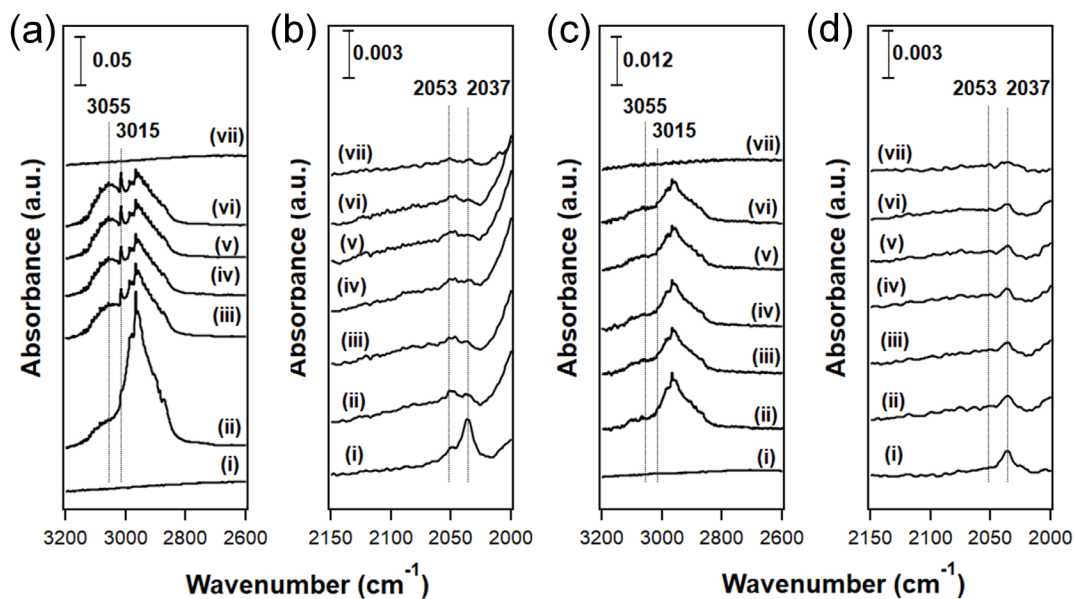
Figure S9. (a, b) FTIR spectra of C_3H_8 treatment on reduced Ga/H-ZSM-5 (Si/Al = 15, Ga/Al = 0.13): (i) before C_3H_8 treatment; (ii-vi) C_3H_8 treatment (1.33 kPa) for 2, 4, 6, 8, and 10 min, respectively; (vii) after evacuation. (c, d) FTIR spectra of C_3H_8 treatment on reduced Ga/H-ZSM-5 (Si/Al = 15, Ga/Al = 0.042): (i) before C_3H_8 treatment; (ii-vi) C_3H_8 treatment (0.27 kPa) for 2, 4, 6, 8, and 10 min, respectively; (vii) after evacuation. The background spectrum was collected in the spectral cell with a dehydrated sample pellet at 550 °C under vacuum.
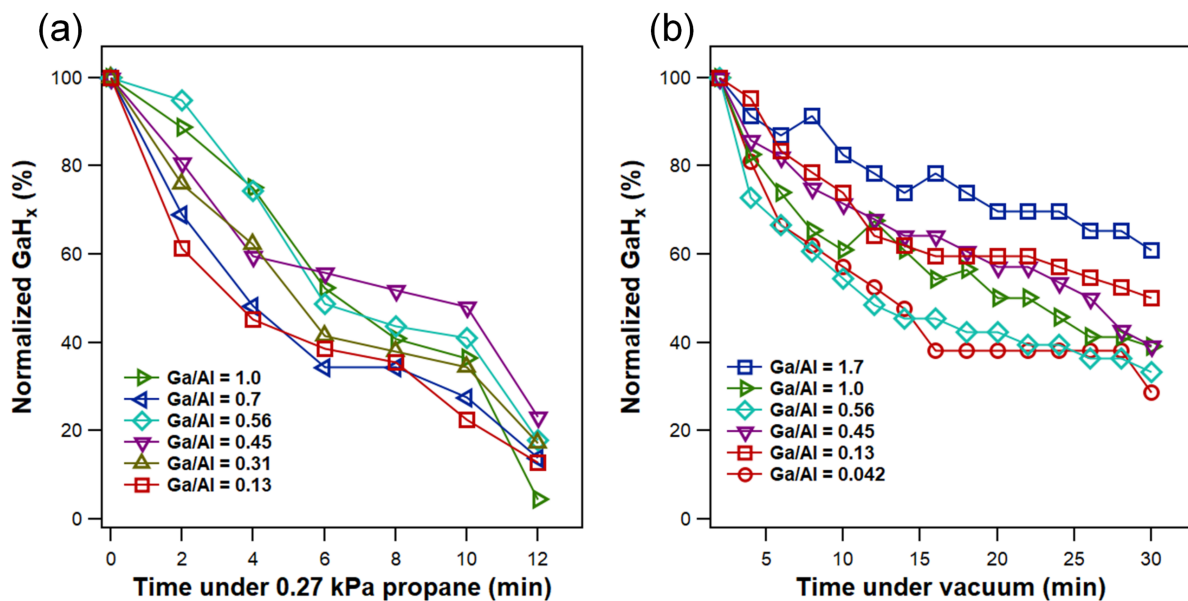
Figure S10. The integrated GaH_x peak area from IR spectra versus time in (a) C_3H_8 (0.27 kPa) and (b) constant vacuum at 550 °C for reduced Ga/H-ZSM-5 with Si/Al ratio of 15 and varying Ga/Al ratios ranging from 0.042 to 1.7. The integrated peak area of GaH_x in (a) was normalized by the GaH_x pea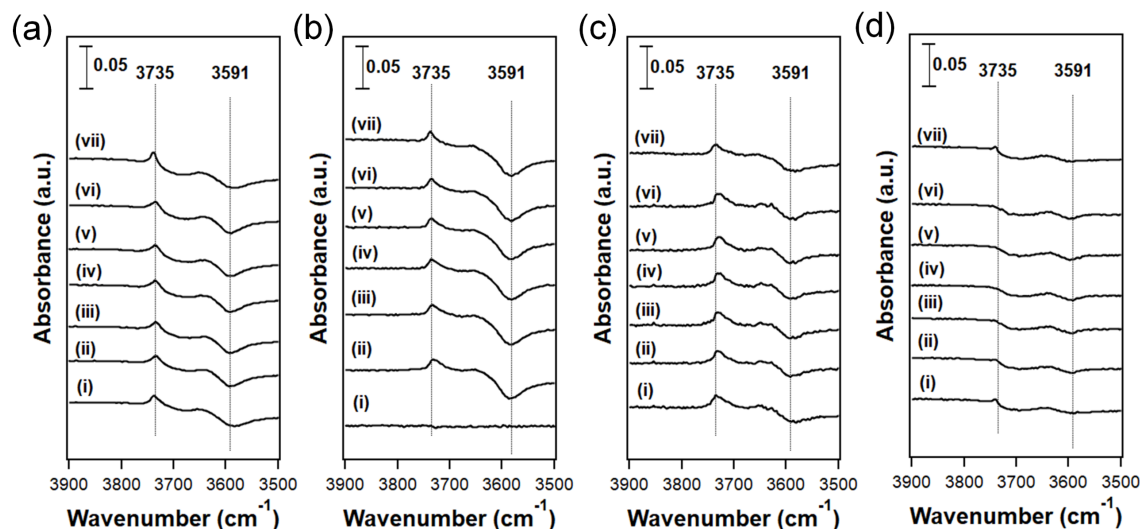k area from the IR spectrum collected during the first 2 min under vacuum after reduction. The point at 12 min represents the GaH_x peak area under vacuum after C_3H_8 treatment. The integrated peak area of GaH_x in (b) was normalized by the GaH_x peak area from the IR spectrum collected during the first 2 min.

Figure S11. FTIR spectra of reduced Ga/H-ZSM-5 (Si/Al = 15, Ga/Al = 0.13) (a): (i) before C_3H_8 treatment; (ii-vi) C_3H_8 treatment (0.27 kPa) for 2, 4, 6, 8, and 10 min, respectively; (vii) after evacuation. (b): (i) before H_2 treatment, (ii-vii) upon evacuating H_2 for 2, 4, 6, 8, 10, and 30 min, respectively. (c): (i) before C_3H_8 treatment; (ii-vi) after C_3H_8 treatment (1.33 kPa) for 2, 4, 6, 8, and 10 min, respectively; (vii) after evacuation. (d) FTIR spectra of C_3H_8 treatment on reduced Ga/H-ZSM-5 (Si/Al = 15, Ga/Al = 0.042): (i) before C_3H_8 treatment; (ii-vi) C_3H_8 treatment (0.27 kPa) for 2, 4, 6, 8, and 10 min, respectively; (vii) after evacuation. The background spectrum was collected in the spectral cell with a dehydrated sample pellet at 550 °C under vacuum.
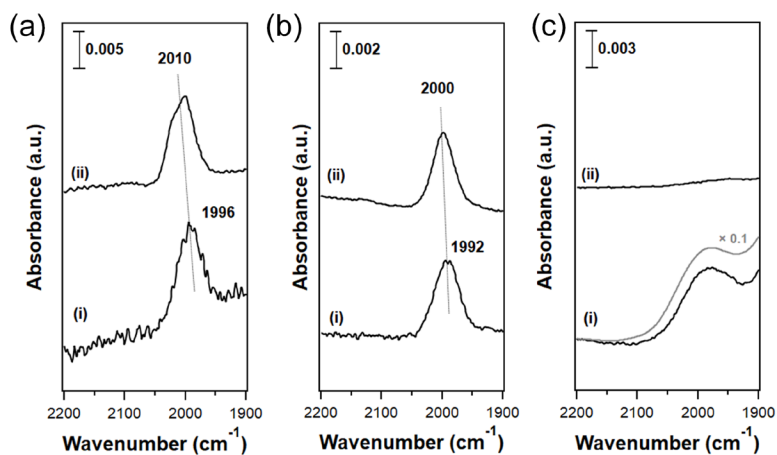
Figure S12. FTIR spectra of reduced (a) Ga_2O_3 and (b) Ga/Al_2O_3 from (i) 550 °C to (ii) 150 °C. (c): reduced (i) Ga/MFI and (ii) Ga/SiO_2 at 550 °C. The background spectrum in was collected in the spectral cell with a dehydrated sample pellet at corresponding temperature under vacuum. Gray traces in (c) were collected at 550 °C after dehydration based on the background spectrum collected in the spectral cell without a sample pellet at the room temperature under vacuum, suggesting that the detected peaks in (c) after reduction is due to the minor change of Si-O-Si structure rather than the formation of GaH_x.
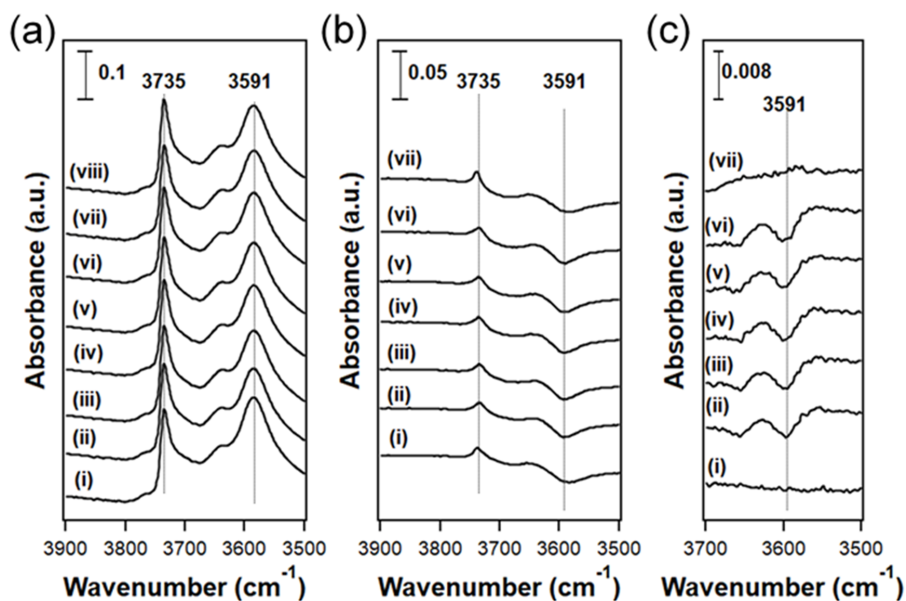
Figure S13. FTIR spectra of C_3H_8 treatment on Ga/H-ZSM-5 (Si/Al = 15 and Ga/Al = 0.13) at 550 °C using different backgrounds: (a) spectra were collected using the background collected in the spectral cell without a sample pellet at the room temperature under vacuum. (i) after dehydration; (ii) after reduction (before C_3H_8 treatment); (iii-vii) C_3H_8 treatment (0.27 kPa) for 2, 4, 6, 8, and 10 min, respectively; (viii) after evacuation. (b) spectra were collected using the background collected in the spectral cell with a sample pellet dehydrated at 550 °C under vacuum: (i) before C_3H_8 treatment; (ii-vi) C_3H_8 treatment (0.27 kPa) for 2, 4, 6, 8, and 1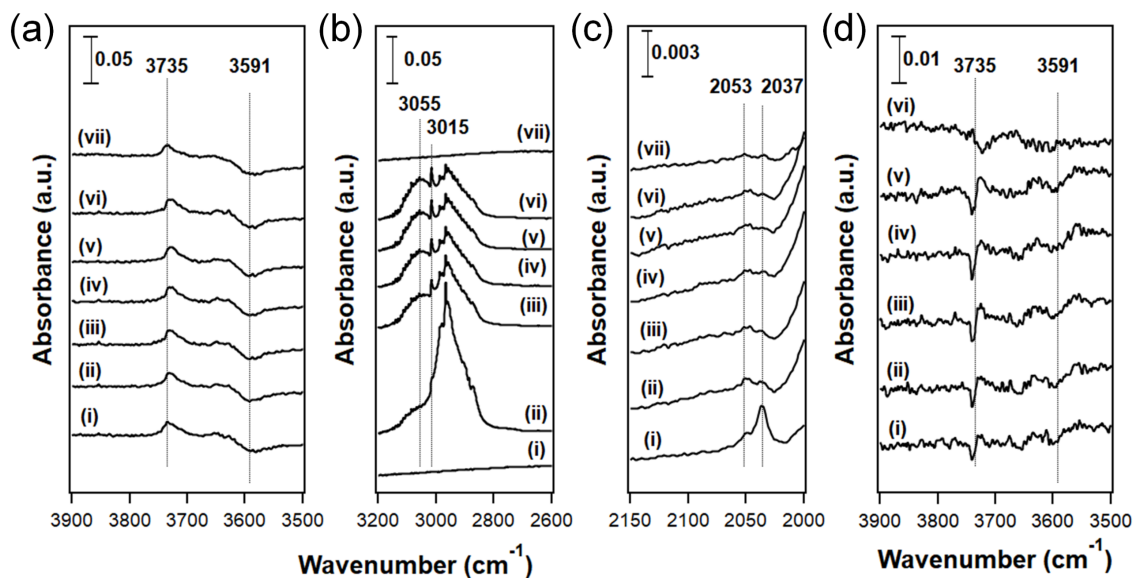0 min, respectively; (vii) after evacuation. (c) spectra were collected using the background collected in the spectral cell with a sample pellet reduced at 550 °C under vacuum: (i) before C_3H_8 treatment; (ii-vi) C_3H_8 treatment (0.27 kPa) for 2, 4, 6, 8, and 10 min, respectively; (vii) after evacuation.

Figure S14. FTIR spectra of (a-c) C_3H_8 treatment on reduced Ga/H-ZSM-5 (Si/Al = 15 and Ga/Al = 0.13) at 550 °C: (i) before C_3H_8 treatment; (ii-vi) C_3H_8 treatment (1.33 kPa) for 2, 4, 6, 8, and 10 min, respectively; (vii) after evacuation. (d) spectra (i-vi) are obtained by subtracting spectrum (i) from spectrum (ii-vii) in (a). The background spectrum was collected in the spectral cell with a sample pellet dehydrated at 550 °C under vacuum.
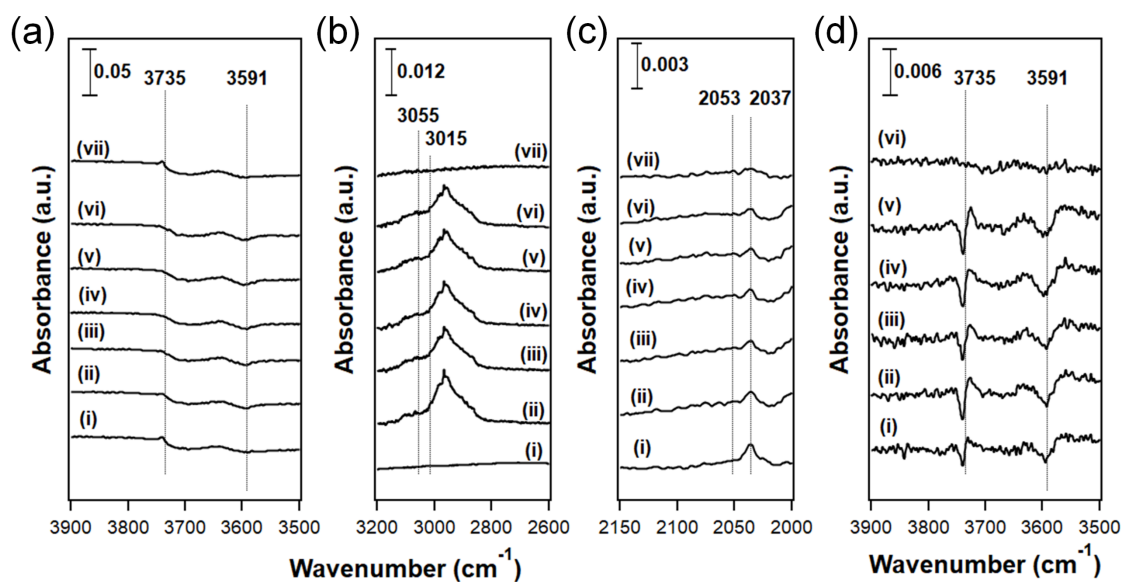
Figure S15. FTIR spectra of (a-c) C_3H_8 treatment on reduced Ga/H-ZSM-5 (Si/Al = 15 and Ga/Al = 0.042) at 550 °C: (i) before C_3H_8 treatment; (ii-vi) C_3H_8 treatment (0.27 kPa) for 2, 4, 6, 8, and 10 min, respectively; (vii) after evacuation. (d) spectra (i-vi) are obtained by subtracting spectrum (i) from spectrum (ii-vii) in (a). The background spectrum was collected in the spectral cell with a sample pellet dehydrated at 550 °C under vacuum.
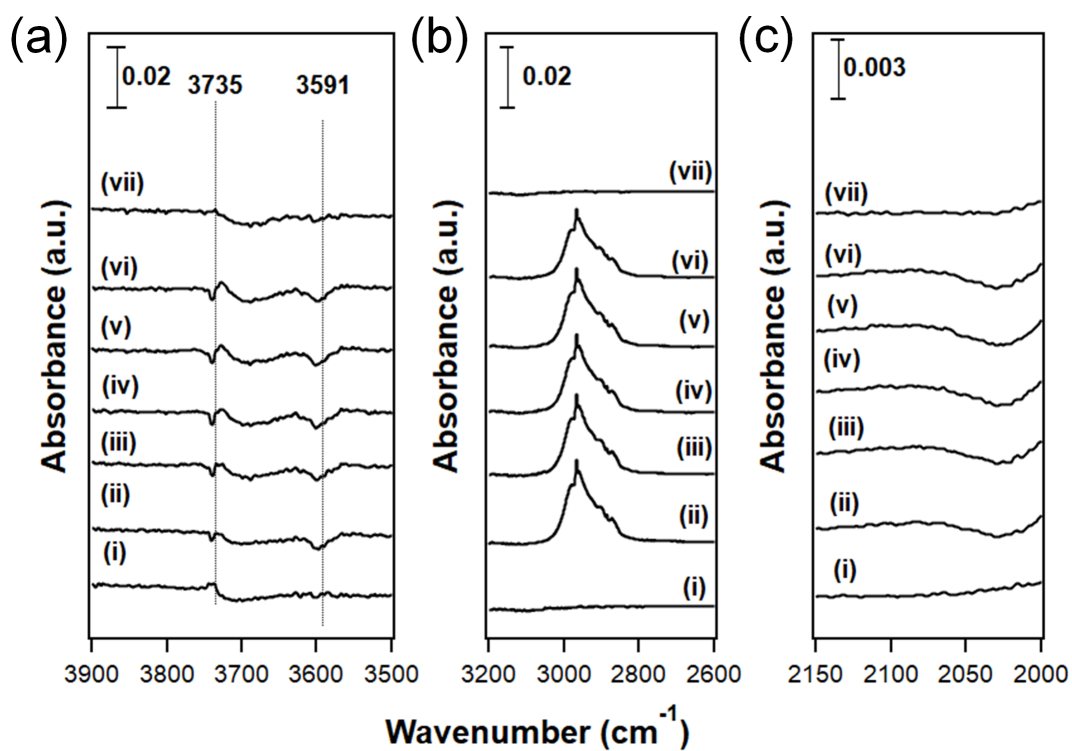
Figure S16. FTIR spectra of C_3H_8 treatment on H-ZSM-5 (Si/Al = 15) at 550 °C in (a) high and (b, c) low wavenumber ranges: (i) before C_3H_8 treatment; (ii-vi) C_3H_8 treatment (0.27 kPa) for 2, 4, 6, 8, and 10 min, respectively; (vii) after evacuation. The background spectrum was collected in the spectral cell with a dehydrated sample pellet at 550 °C under vacuum.
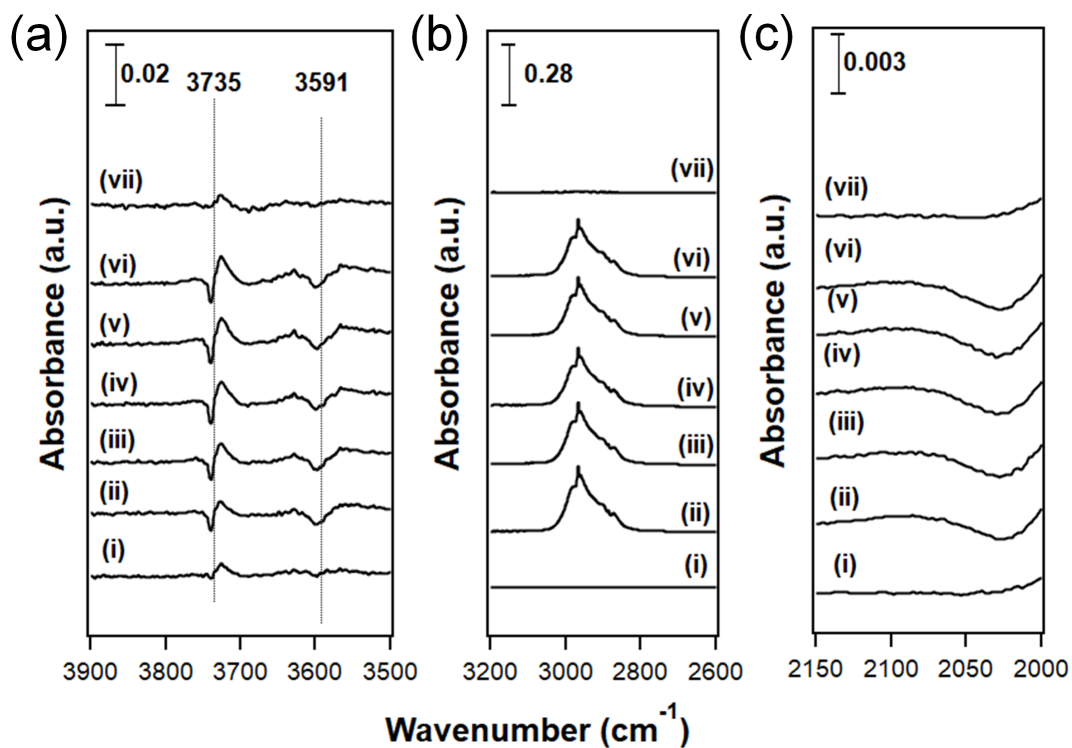
Figure S17. FTIR spectra of C_3H_8 treatment on H-ZSM-5 (Si/Al = 15) at 550 °C in (a) high and (b, c) low wavenumber ranges: (i) before C_3H_8 treatment; (ii-vi) C_3H_8 treatment (1.33 kPa) for 2, 4, 6, 8, and 10 min, respectively; (vii) after evacuation. The background spectrum is collected in the spectral cell with a dehydrated sample pellet at 550 °C under vacuum.
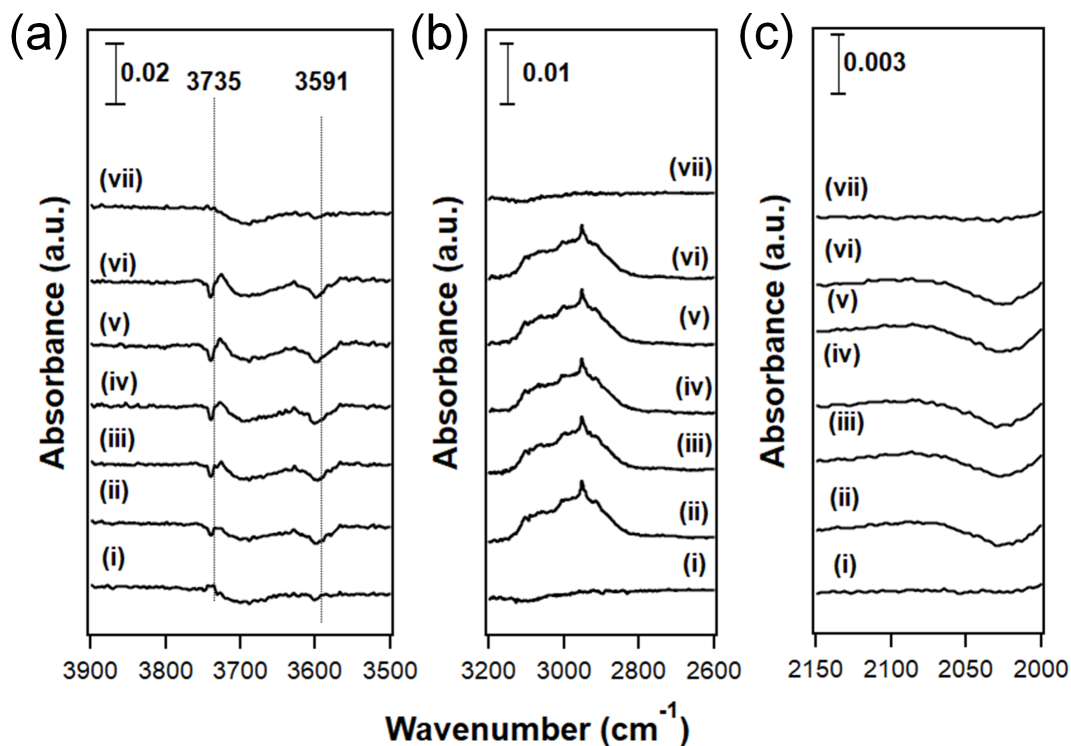
Figure S18. FTIR spectra of C_3H_6 treatment on H-ZSM-5 (Si/Al = 15) at 550 °C in (a) high and (b, c) low wavenumber ranges: (i) before C_3H_6 treatment; (ii-vi) C_3H_6 treatment (0.27 kPa) for 2, 4, 6, 8, and 10 min, respectively; (vii) after evacuation. The background spectrum is collected in the spectral cell with a dehydrated sample pellet at 550 °C under vacuum.
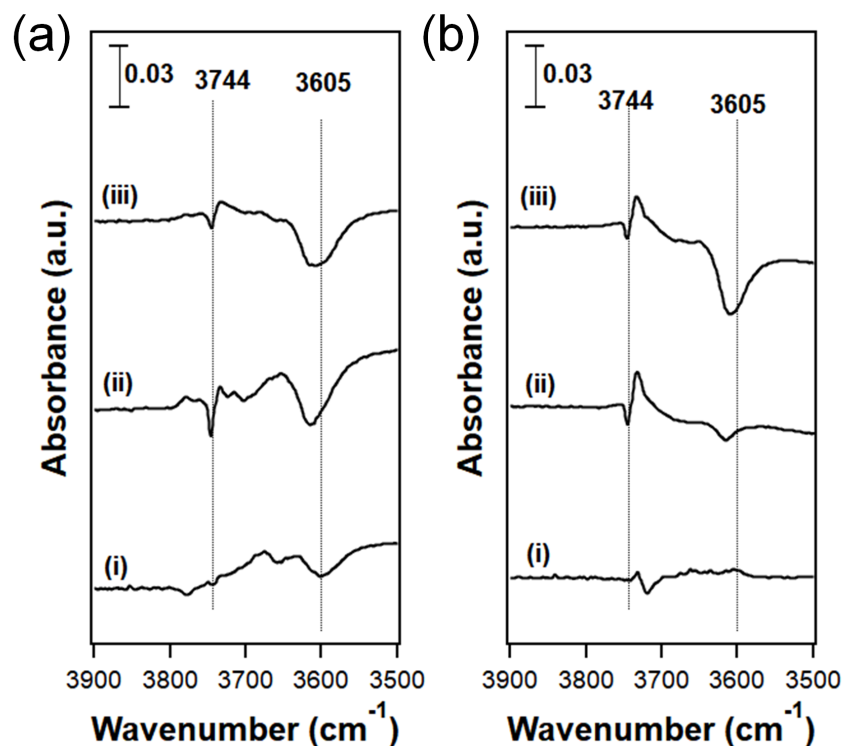
Figure S19. FTIR spectra (OH region) of Ga/H-ZSM-5 cooling in the presence of C_3H_8 at 150 °C: (a) H-ZSM-5 (Si/Al = 15) with Ga/Al ratios of (i) 0, (ii) 0.042, (iii) 0.13 and (b) H-ZSM-5 (Si/Al = 39) with Ga/Al ratios of (i) 0, (ii) 0.12, (iii) 0.44. The background spectrum was collected in the spectral cell with a sample pellet dehydrated at 550 °C and cooled down to 150 °C under vacuum.
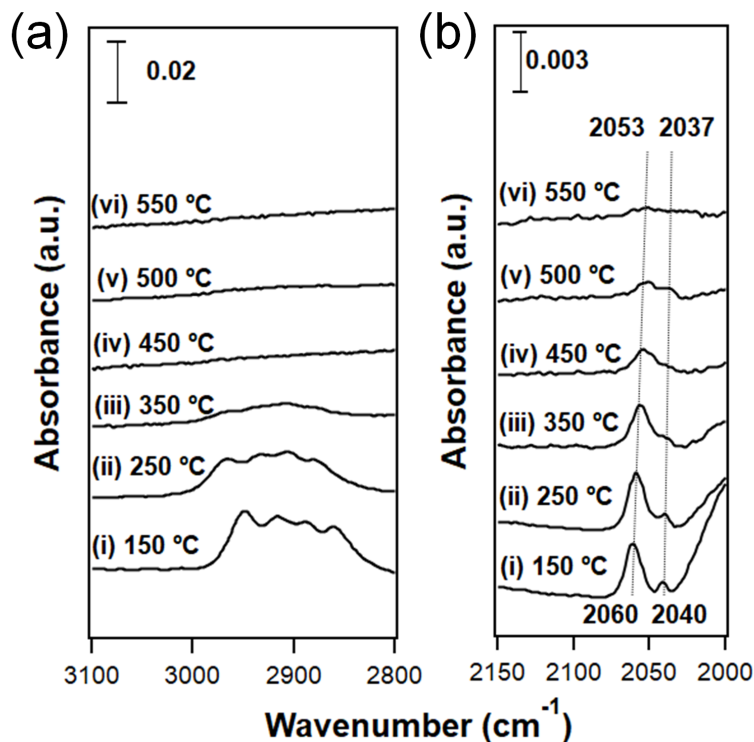
Figure S20. FTIR spectra of thermal treatment on C_3H_8 treated Ga/H-ZSM-5 (Si/Al = 15, Ga/Al = 0.13) from 150 to 550 °C (indicated in the figure legends) in (a) high and (b) low wavenumber ranges. The samples were reduced at 550 °C, and cooled down under 1.33 kPa C_3H_8 to 150 °C, followed by evacuation. The background spectrum is collected with the sample at the corresponding temperature under vacuum after dehydration.

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