Electronic Supplementary Material (ESI) for Reaction Chemistry & Engineering.

Supplementary Information

In situ FTIR spectroscopy study to reveal Ga modified ZSM-5 for boosting isobutene amination

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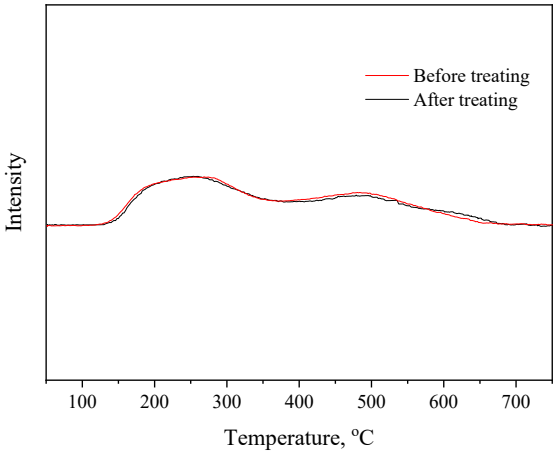
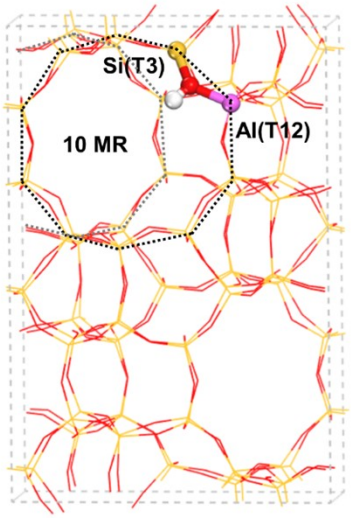


Fig. S1 NH_3-TPD



Framework	ZSM-5
Formal composition	$Si_{96}O_{192}$
Acid site	Al(T12)-OH-Si(T3)
Ring sizes	10-ring
Pore size	5.3 × 5.6 Å
Si/Al ratio	95

Fig. S2 Geometry structures of H-ZSM-5 for DFT calculation. Yellow: silicon; red: oxygen; purple: aluminum; white: hydrogen; gray: carbon. 10 MR means 10-membered-ring. T represents the tetrahedral Si and Al atom.

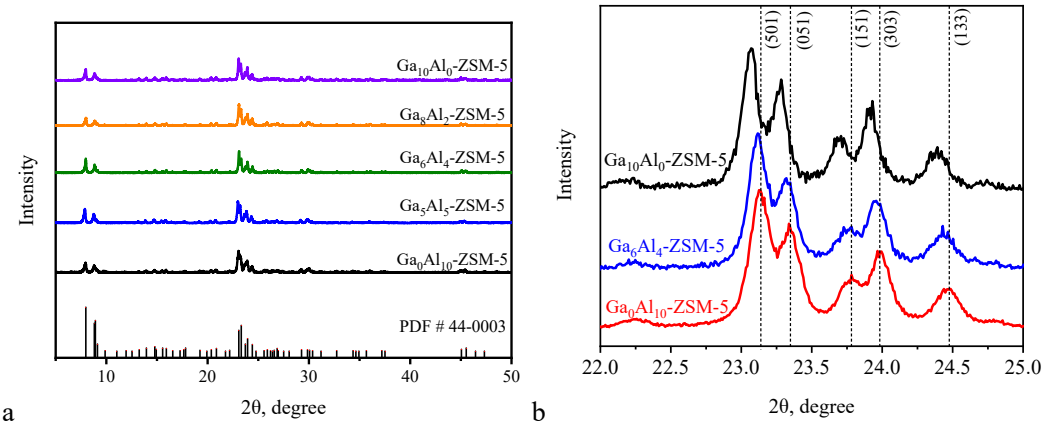


Fig. S3 (a) XRD patterns of the catalysts. (b) XRD patterns of $Ga_{10}Al_0$-ZSM-5, Ga_6Al_4-ZSM-5, and Ga_0Al_{10}-ZSM-5 in 2θ range of 22°-25°.

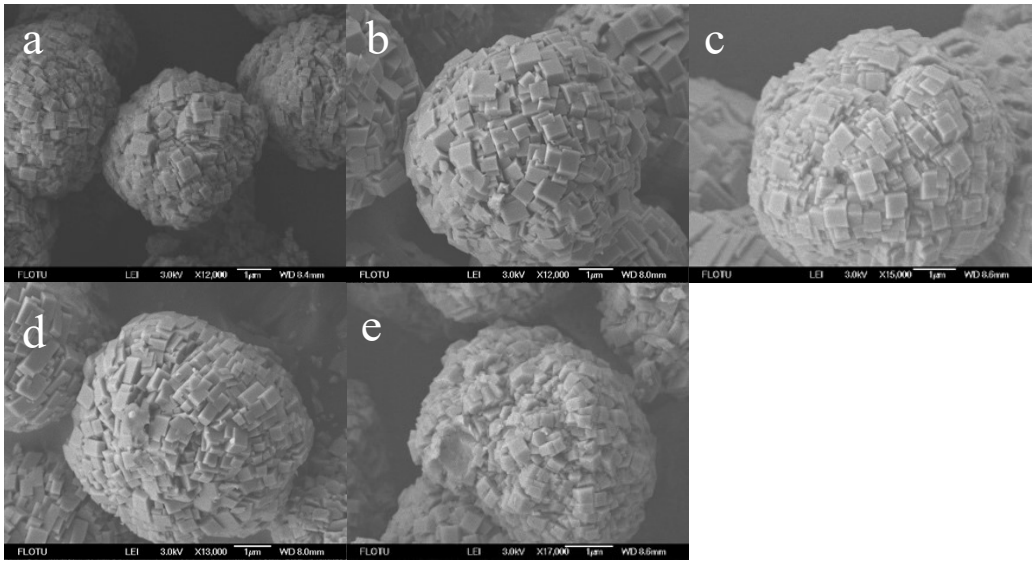


Fig. S4 SEM images of Ga_xAl_y-ZSM-5 catalysts. **(a)** Ga_0Al_{10}-ZSM-5. **(b)** Ga_5Al_5-ZSM-5. **(c)** Ga_6Al_4-ZSM-5. **(d)** Ga_8Al_2-ZSM-5. **(e)** $Ga_{10}Al_0$-ZSM-5.

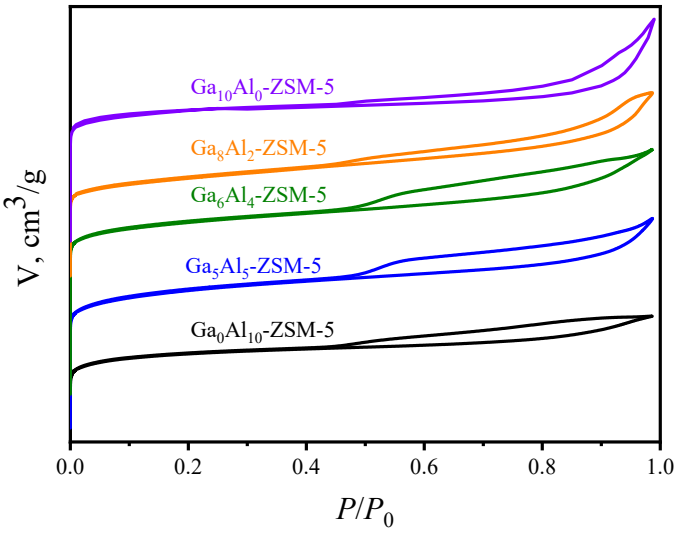


Fig. S5 N_2 adsorption-desorption isotherms of the catalysts.

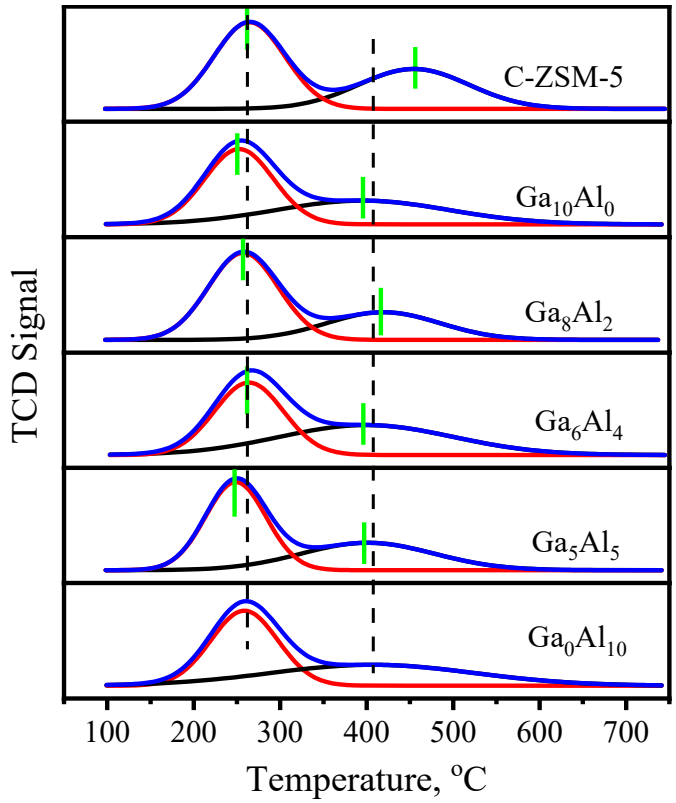


Fig. S6 NH_3-TPD profiles of the catalysts.

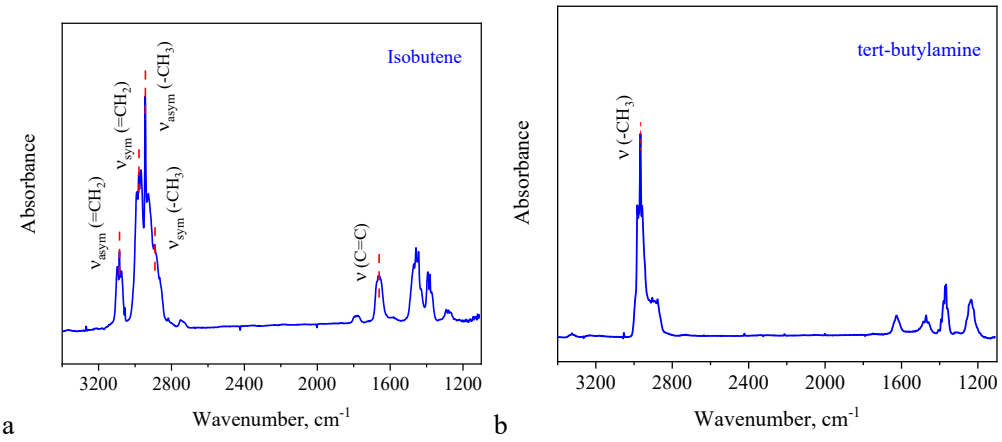


Fig. S7 IR spectra of the gas phase chemicals and corresponding vibration.

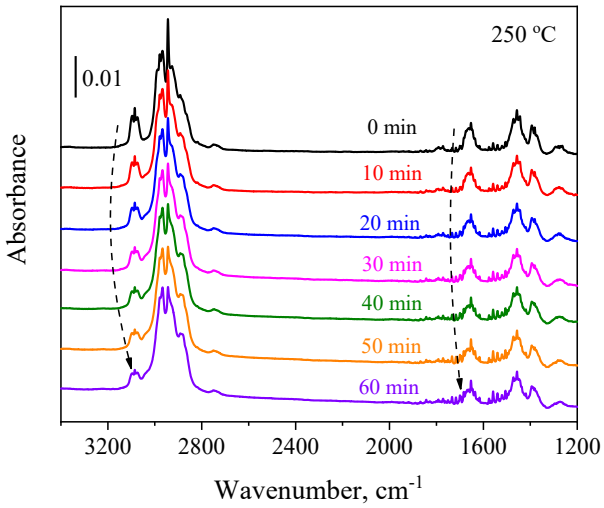


Fig. S8 Evolution of in situ FTIR spectra for isobutene protonation over Ga_6Al_4-ZSM-5.

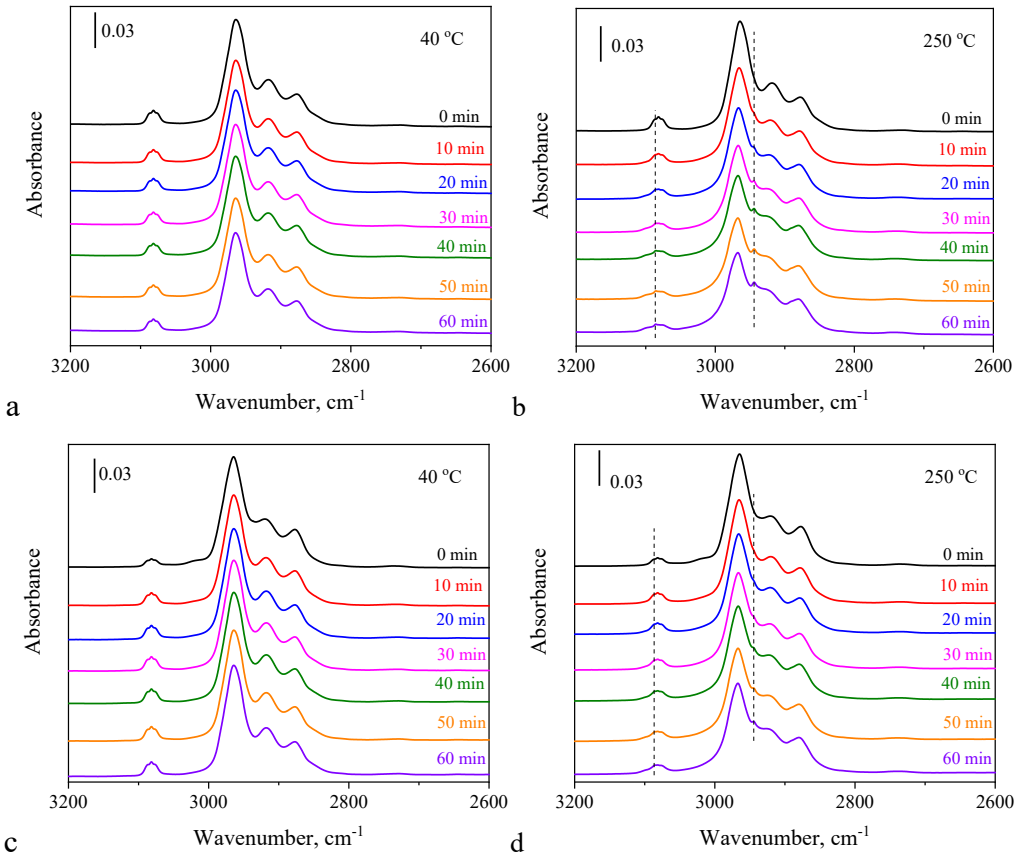


Fig. S9 Dynamic changes of in situ FTIR spectra for the chemicals over Ga_6Al_4-ZSM-5. (a) 2,4,4-trimethyl-1-pentene at 40 ºC. **(b)** 2,4,4-trimethyl-1-pentene at 250 ºC. **(c)** 2,4,4-trimethyl-2-pentene at 40 ºC. **(d)** 2,4,4-trimethyl-2-pentene at 250 ºC.

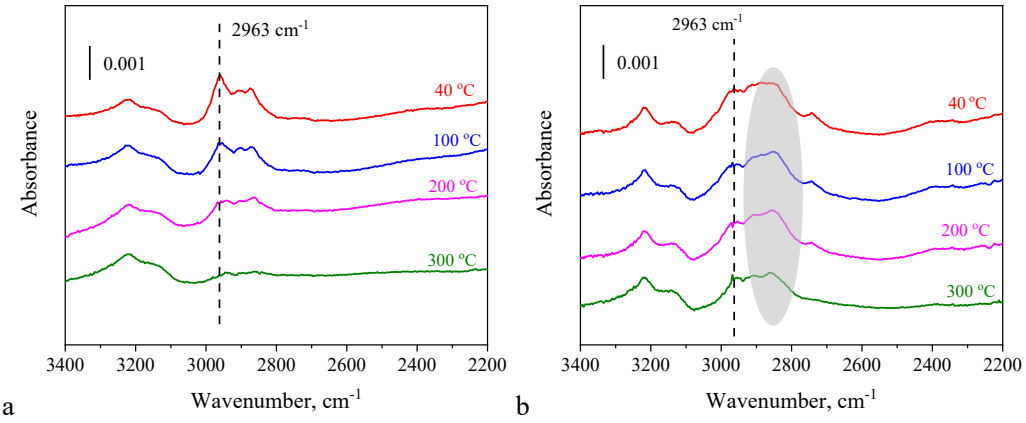


Fig. S10 Desorption of surface species over Ga_6Al_4-ZSM-5. (a) after in situ FTIR experiment of C8-1 at 40 °C. **(b)** after in situ FTIR experiment of C8-1 at 250 °C.

After in situ FTIR experiment of C8-1 for 60 min (as shown in **Fig. S9**), the temperature of the catalyst was first set to 40 °C and then the IR cell was evacuated by a turbo pump to remove the gas phase. With the pressure decreasing to 5×10^{-3} Pa, IR was collected as the spectrum of 40 °C. After that, the temperature of the catalyst was set to desired value (*T*) and kept for 1 min and then was set back to 40 °C to collect the IR spectra of *T*.

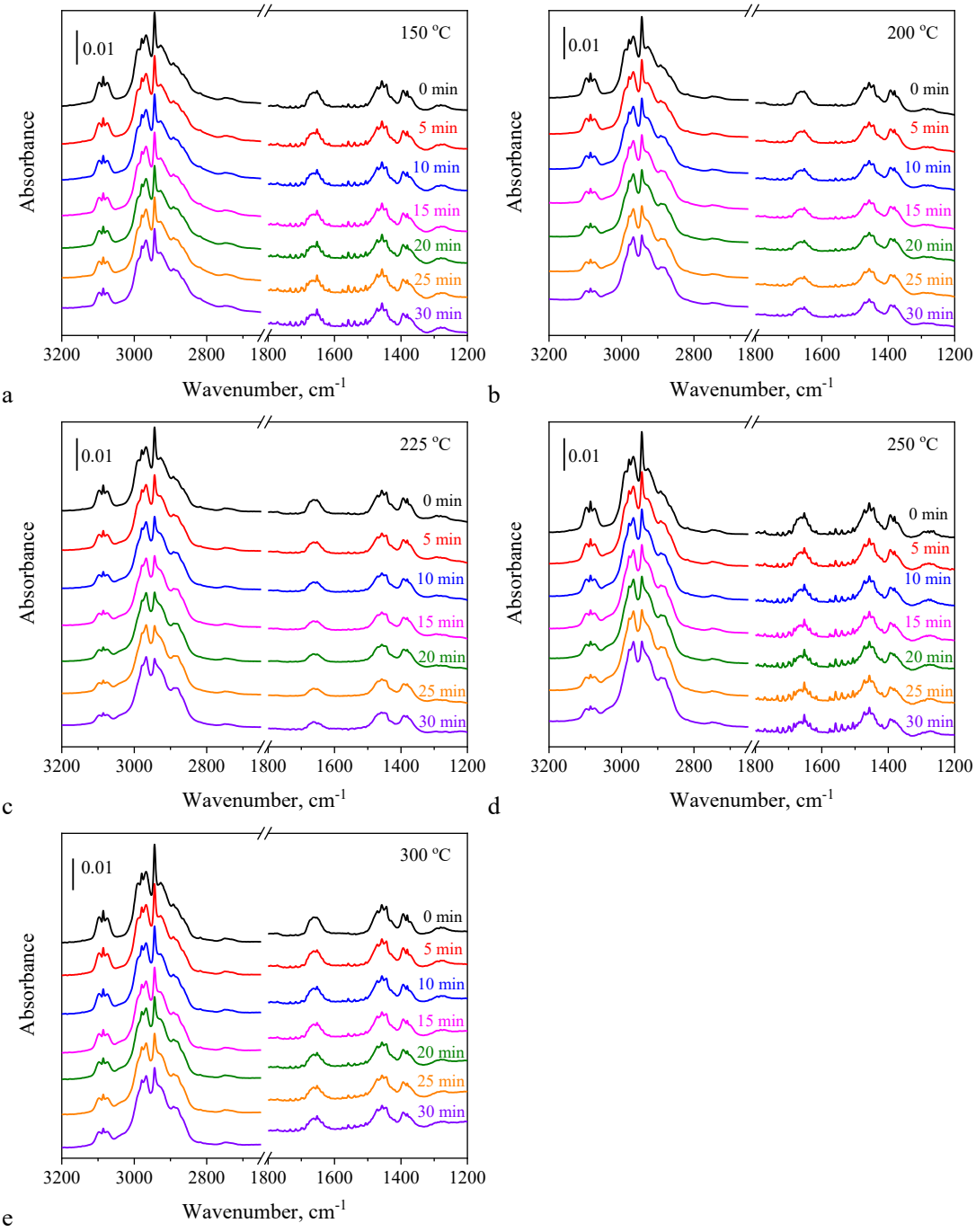


Fig. S11 In situ FTIR spectra of isobutene protonation over Ga_6Al_4-ZSM-5 at different temperature. (a) 150 °C. **(b)** 200 °C. **(c)** 225 °C. **(d)** 250 °C. **(e)** 300 °C.

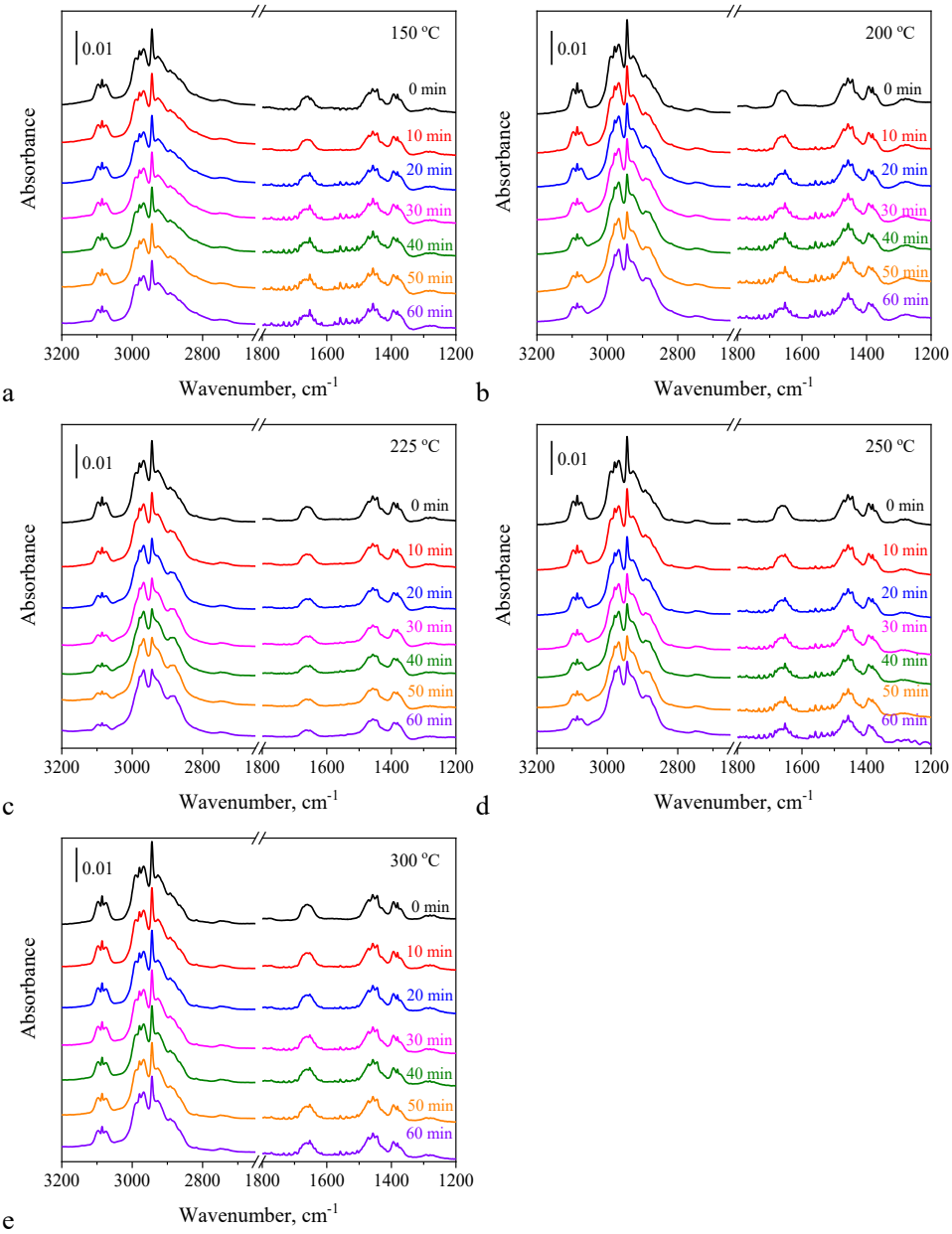


Fig. S12 In situ FTIR spectra of isobutene protonation over $Ga_{10}Al_0$-ZSM-5 at different temperature. (a) 150 °C. **(b)** 200 °C. **(c)** 225 °C. **(d)** 250 °C. **(e)** 300 °C.

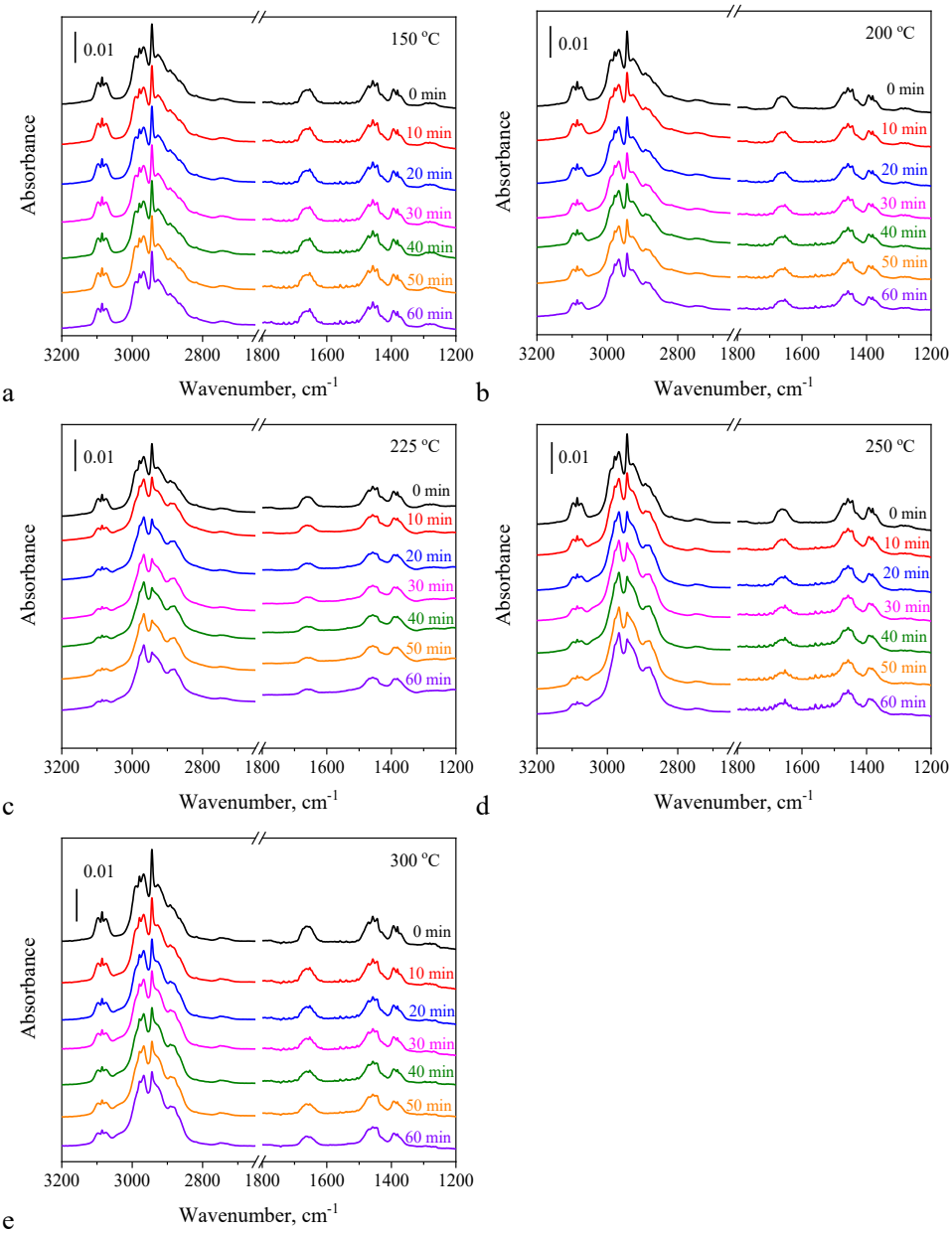


Fig. S13 In situ FTIR spectra of isobutene protonation over Ga_0Al_{10}-ZSM-5 at different temperature. (a) 150 °C. **(b)** 200 °C. **(c)** 225 °C. **(d)** 250 °C. **(e)** 300 °C.

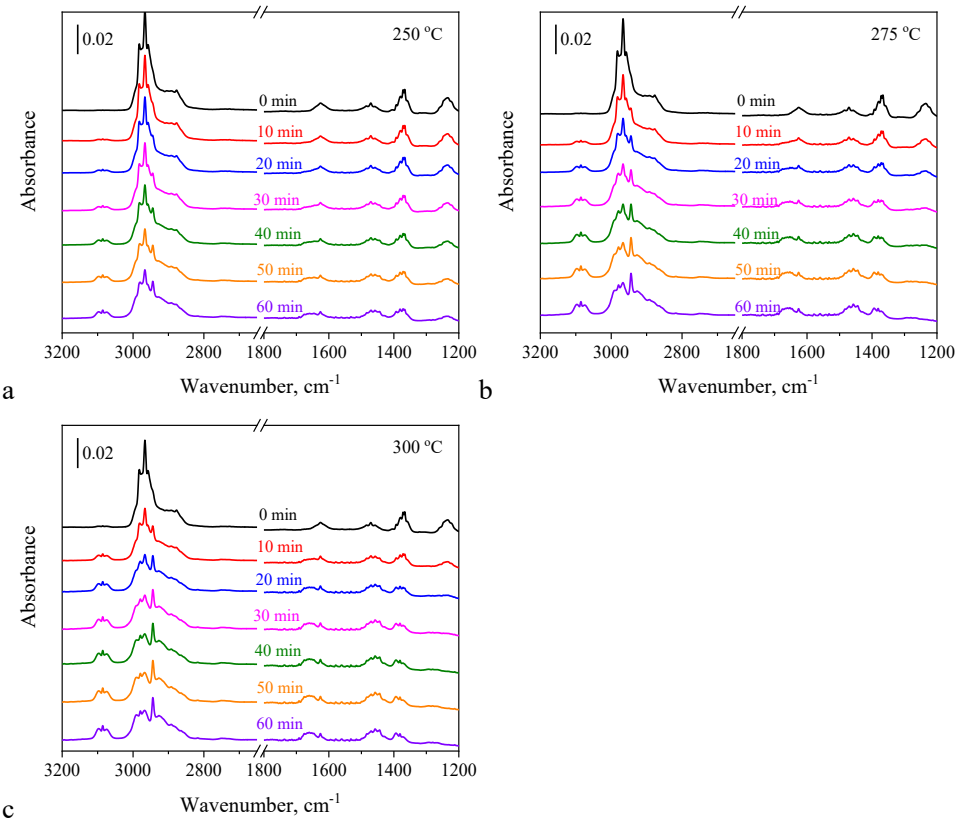


Fig. S14 In situ FTIR spectra of Hoffman elimination over Ga_6Al_4-ZSM-5 at different temperature. (a) 250 °C. **(b)** 275 °C. **(c)** 300 °C.

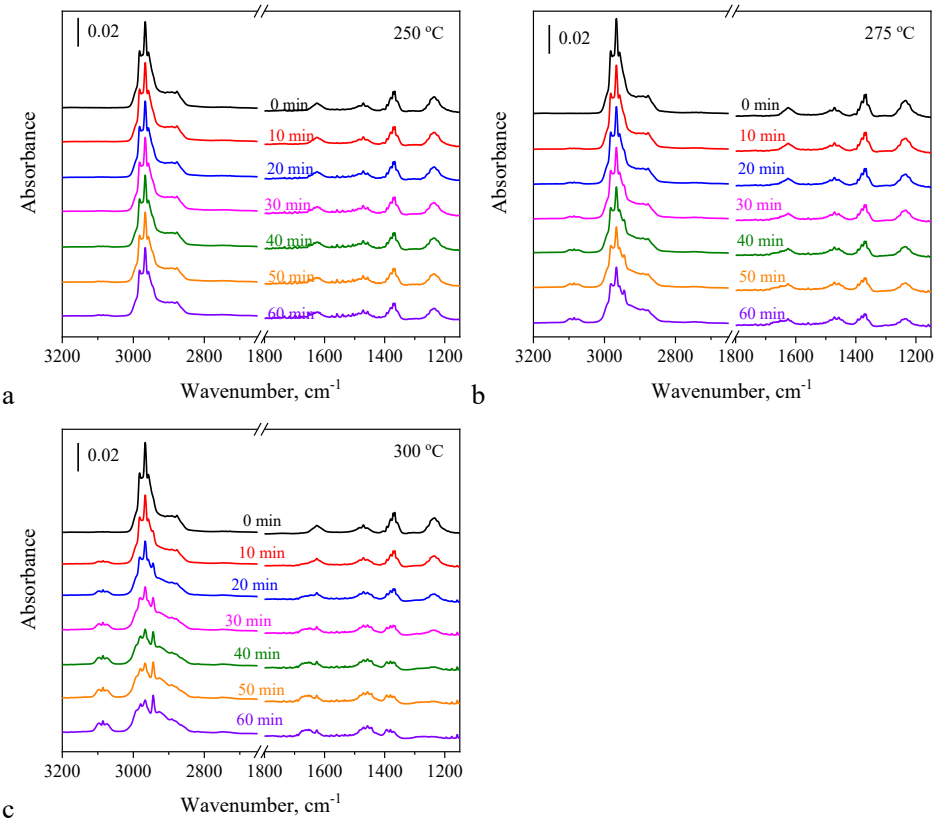


Fig. S15 In situ FTIR spectra of Hoffman elimination over $Ga_{10}Al_0$-ZSM-5 at different temperature. (a) 250 °C. **(b)** 275 °C. **(c)** 300 °C.

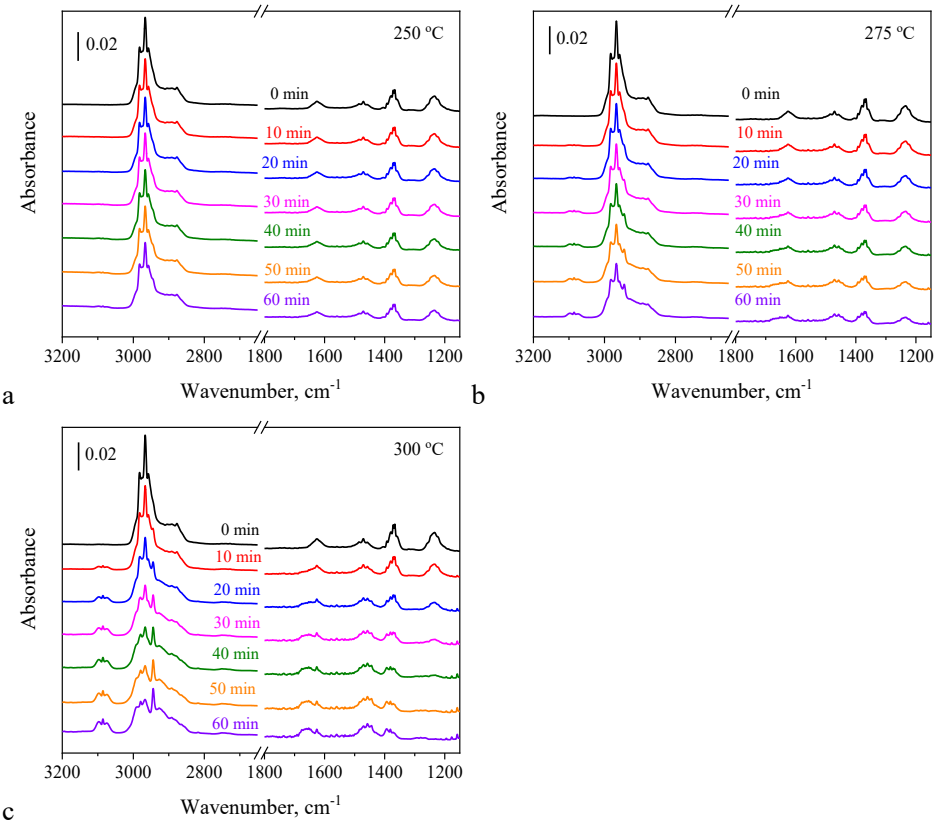
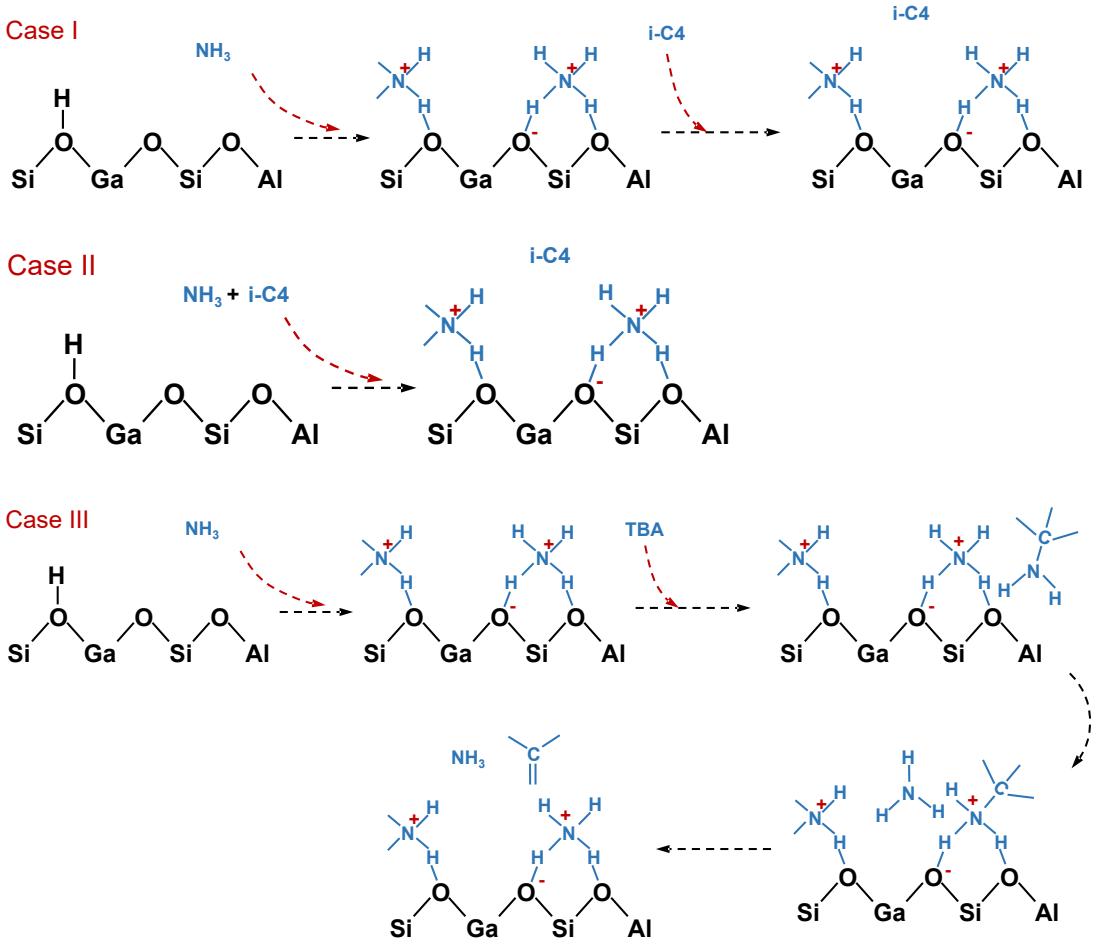
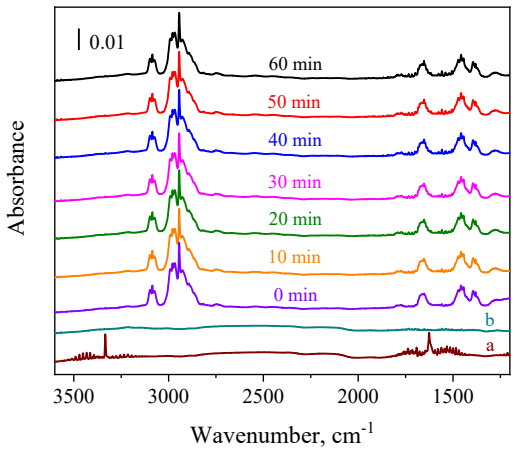


Fig. S16 In situ FTIR spectra of Hoffman elimination over Ga_0Al_{10}-ZSM-5 at different temperature. (a) 250 °C. **(b)** 275 °C. **(c)** 300 °C.

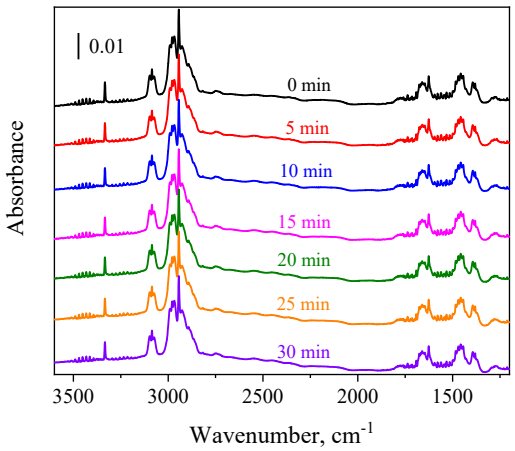
a


Case I
NH3
i-C4
Case II
NH3 + i-C4
Case III
TBA
Si
Ga
Al

b


0.01
60 min
50 min
40 min
30 min
20 min
10 min
0 min
b
a
Absorbance
3500
3000
2500
2000
1500
Wavenumber, cm-1

c


0.01
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Absorbance
3500
3000
2500
2000
1500
Wavenumber, cm-1

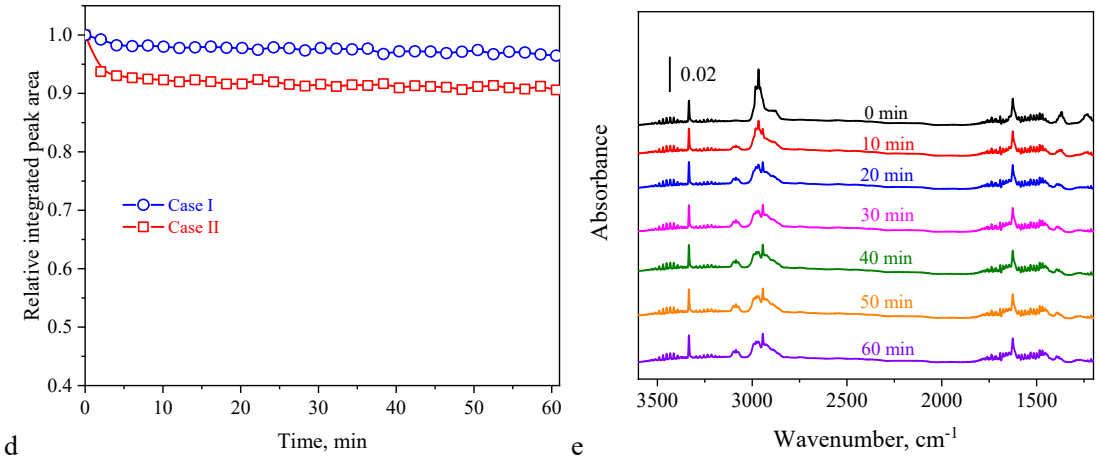


Fig. S17 Investigation of the relative adsorption stability of the chemicals. (a) schemes of the cases. **(b)** the in situ FTIR spectra of case I (T = 250 °C). **(c)** the in situ FTIR spectra of case II (T = 250 °C). **(d)** the integrated peak area of band at 3050-3125 cm^{-1} of case I and II. **(e)** the in situ FTIR spectra of case III (T = 300 °C).

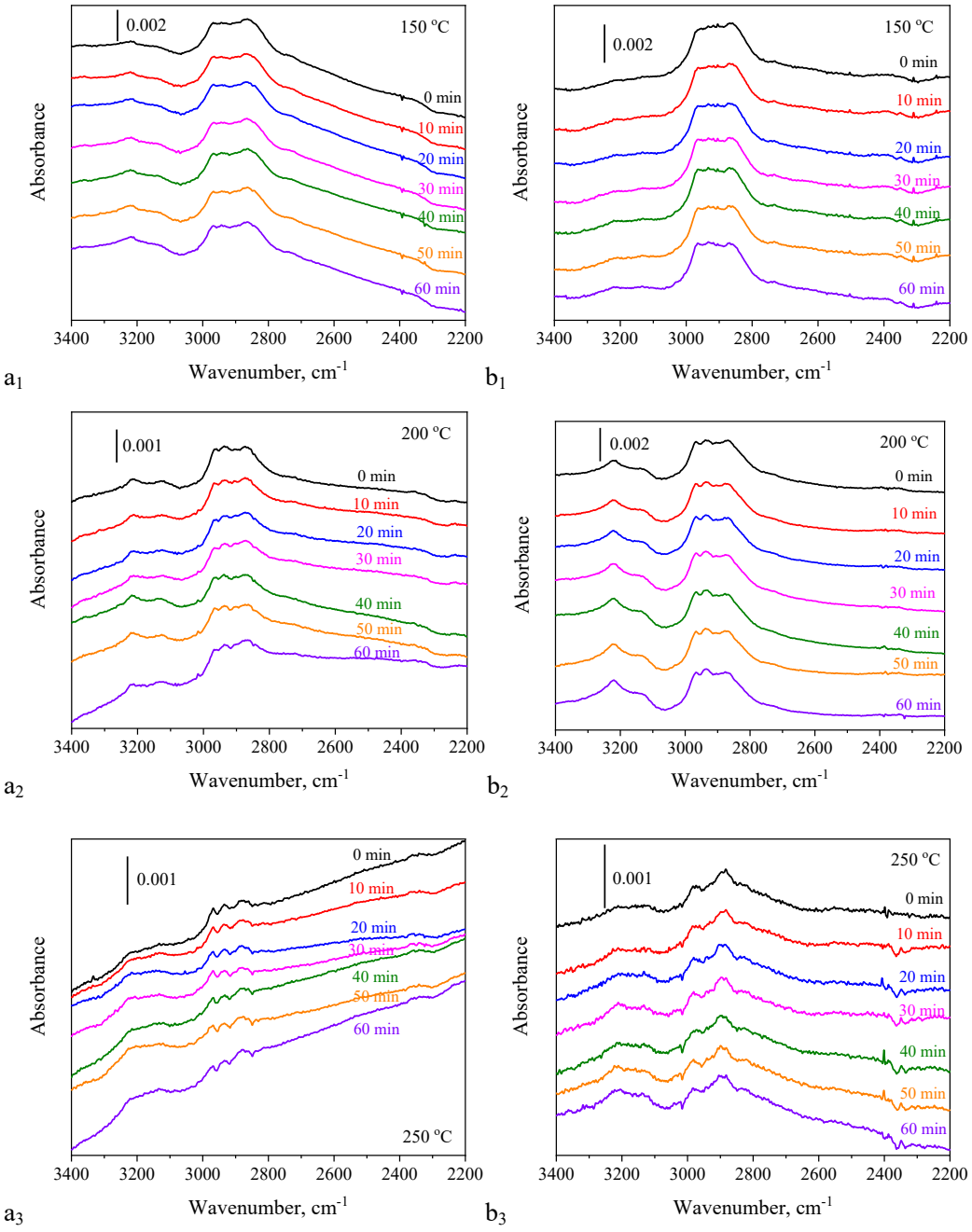
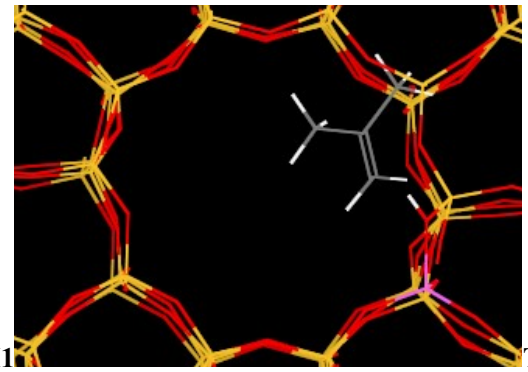
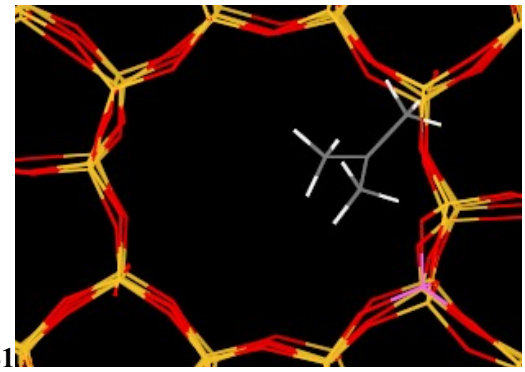


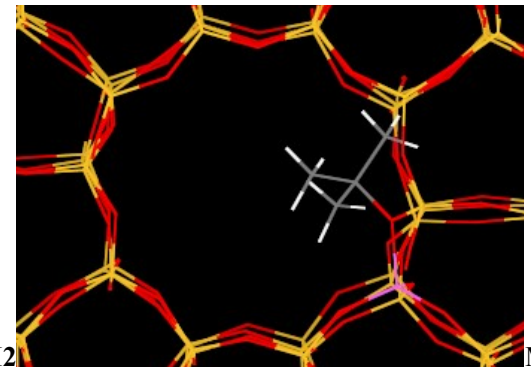
Fig. S18 In situ FTIR dynamic changes of alkoxide. (a) under 4 kPa NH_3 atmosphere at 150 °C (a_1), 200 °C (a_2), and 250 °C (a_3). **(b)** under He atmosphere at 150 °C (b_1), 200 °C (b_2), and 250 °C (b_3).



M1



TS1



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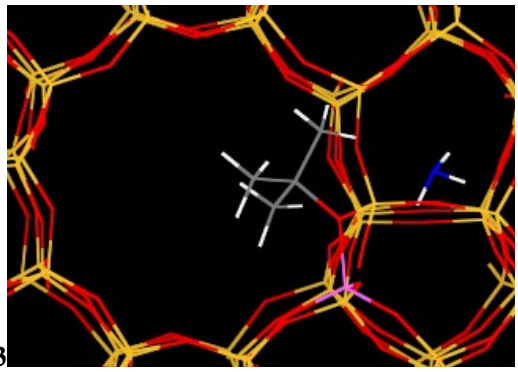

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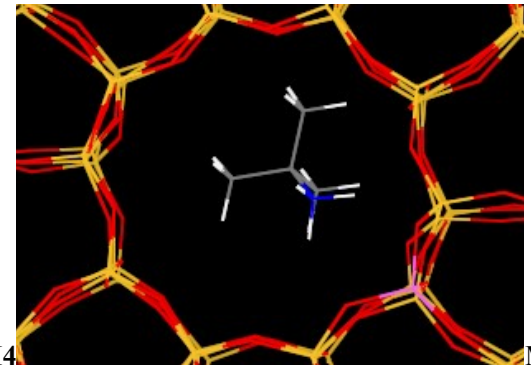

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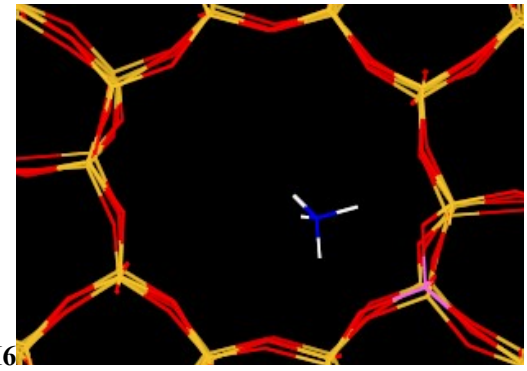

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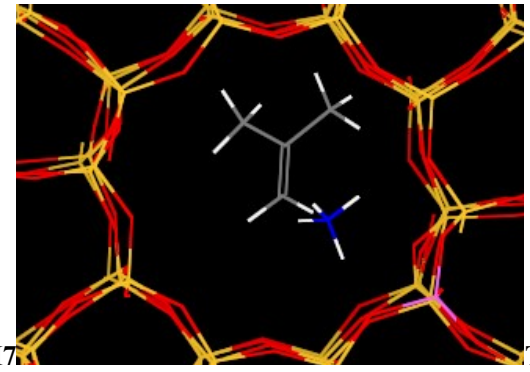

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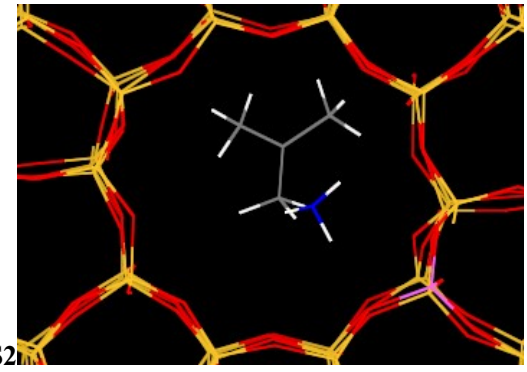
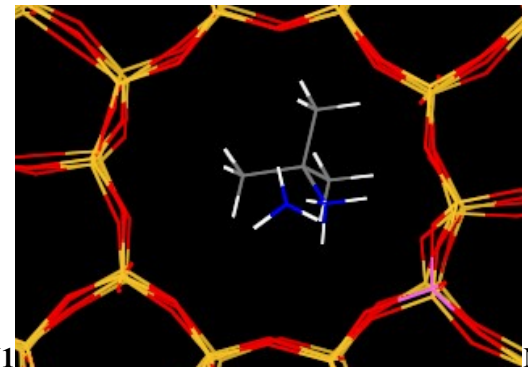


TS2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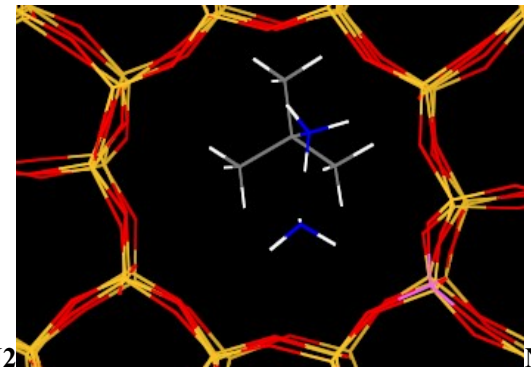
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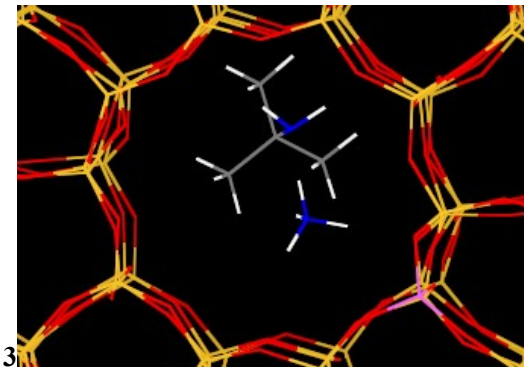
3

Fig. S19 Geometry structures of the intermediates along reaction coordinate over ZSM-5.

Table S1. Characterization of the catalysts.

Samples	[a]Si/(Al+Ga)	[b]Surface area, m^2/g	[c]Acid amount, mmol/g
Ga_0Al_{10}-ZSM-5	18.1	367	0.285
Ga_5Al_5-ZSM-5	20.2	326	0.285
Ga_6Al_4-ZSM-5	17.5	306	0.256
Ga_8Al_2-ZSM-5	21.0	302	0.214
$Ga_{10}Al_0$-ZSM-5	21.3	241	0.380

[a]. Measured by XRF; [b]. Calculated by BET and t-plot methods; [c]. Mid-strong acid amount measured by NH_3-TPD between 350 and 650 °C.

Table S2. Adsorption energy of the chemicals over Al-MFI and Ga-MFI.

Model	NH_3/eV	IBE/eV	TBA/eV
Ga-12T	-1.43	-1.08	-2.48
Al-12T	-1.47	-1.09	-2.52