SUPPORTING INFORMATION

Relationship between ZSM-5 pore modifications and gallium proximity and liquid hydrocarbon number distribution from ethanol oligomerization

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Figure S1: The BJH pore size distribution curves derived from N_2 adsorption-desorption studies for Ga(5 wt.%)/ZSM-5 and Ga(5 wt.%)/modified-ZSM-5 catalysts.

Figure S2: Effect of Ga loading on ZSM-$5_{0.8M}$ support porosity and surface area.

Figure S3: (a) STEM images of Ga(5 wt.%)/ZSM-5, (b) Ga, and (c) overlaid Ga/Si/Al elemental mapping. STEM images of (d) Ga(5%)/ZSM-$5_{0.8M}$, (e) Ga, and (f) overlaid Ga/Si/Al elemental mapping.

Figure S4: Ga average particle diameters in Ga(5 wt.%)/ZSM-5 and Ga(5 wt.%)/ZSM-$5_{0.8M}$.

Table S1: ICP-OES analysis for the liquid fraction collected after treating ZSM-5 with 0.2, 0.6, 0.8, & 1.0M NaOH.

Table S2: ICP-OES analysis for Ga (5 wt.%)/ZSM-$5_{0.8M}$ catalysts synthesized at different times.

Table S3: XPS derived Si/Ga surface ratios of as-synthesized samples.

Figure S5: Ga 2p3/2 XPS spectra of 2, 5, and 8 wt.% gallium loadings for 4-, 16- and 32-hours Ga wet-impregnation synthesis times.

Figure S6: H_2-TPR profiles for Ga(5 wt.%)/ZSM-5 and Ga(5 wt.%)/ZSM-5_{xM} catalysts

Table S4: H_2-TPR composition data for each gallium oxide species (nano-Ga_2O_3, GaO^+, and EF-Ga_2O_3) quantified from their peak areas.

Figure S7: NH_3-TPD profiles of Ga(5 wt.%)/ZSM-5 and Ga(5 wt.%)/ZSM-5_{xM} (xM = 0.2, 0.6, 0.8 &1.0M).

Figure S8: The effect of temperature on ethanol oligomerization over Ga(5 wt.%)/ZSM-5 and Ga(5%)/ZSM-5_{xM} catalysts at 1.6h^{-1} WHSV.

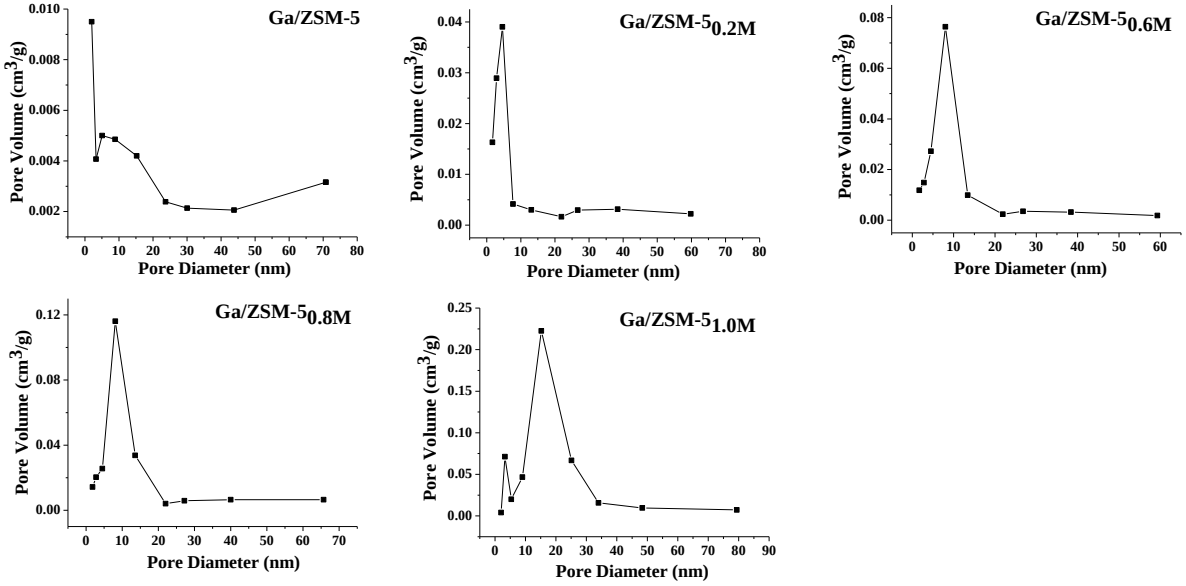
Figure S9: X-ray diffraction spectra of fresh Ga/ZSM-$5_{0.8M}$ (blue color) and used Ga/ZSM-$5_{0.8M}$ after reacting pure ethanol (red color) and 40% wet-ethanol feed (black color) to form hydrocarbons.

Figure S10: (a) N_2 adsorption-desorption isotherms and (b) surface area (SA), external surface area, and micropore surface area for fresh Ga(5 wt.%)/ZSM-$5_{0.8M}$ and used Ga(5 wt.%)/ZSM-$5_{0.8M}$ catalysts. (c) Pore volumes for fresh Ga(5 wt.%)/ZSM-$5_{0.8M}$ and used Ga(5 wt.%)/ZSM-$5_{0.8M}$ catalysts.

Figure S11: NH_3-TPD profiles of fresh catalyst and used catalysts for pure ethanol and wet ethanol.

Figure S12: Effect of pore structure on product selectivities and LHYs for reaction of ethanol on ZSM-5, Beta zeolite, and Y-zeolite catalysts at 350°C and a $0.4h^{-1}$ SV.

H_2-TPR and TPO: H_2-Temperature program reduction (TPR) and temperature program oxidation (TPO) experiments were conducted with a Hiden Analytical CATLAB instrument (2375 Maxwell Lane, Sedona, AZ 86336). For H_2-TPR experiments, a 100mg sample was dried in a 2% O_2/He stream for 1 h at 450°C and then cooled to 150 °C prior to analysis. Then the sample was reduced in a 10% H_2/He (50 mL/min) stream at a heating rate of 10°C/min to 950°C. TPO characterization techniques were applied in the same system to about 100mg of catalysts that had been used for ethanol and wet-ethanol streams. Prior to analysis, the samples were dried in a 2% O_2/He stream (30 mL/min) at 150°C for 1 h, followed by heating at a ramp up rate of 10°C/min to 950°C. Peaks for CO_2 (m/z = 44), CO (m/z = 28), and H_2O (m/z = 18) were recorded with a mass spectrometer (Hiden Quadrupole, 2375 Maxwell Lane, Sedona, AZ 86336).



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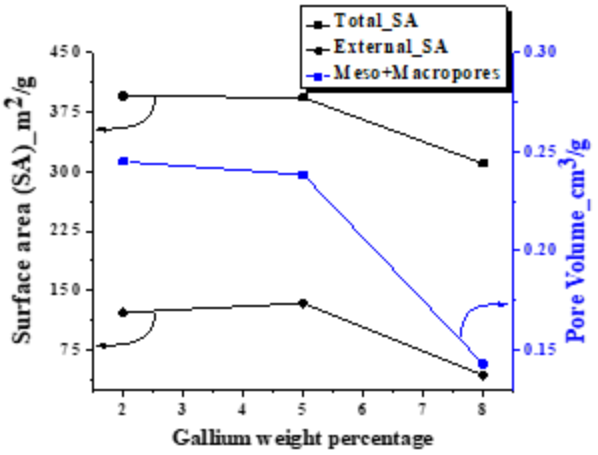


Figure S2: Effect of Ga loading on ZSM-$5_{0.8M}$ support porosity and surface area.

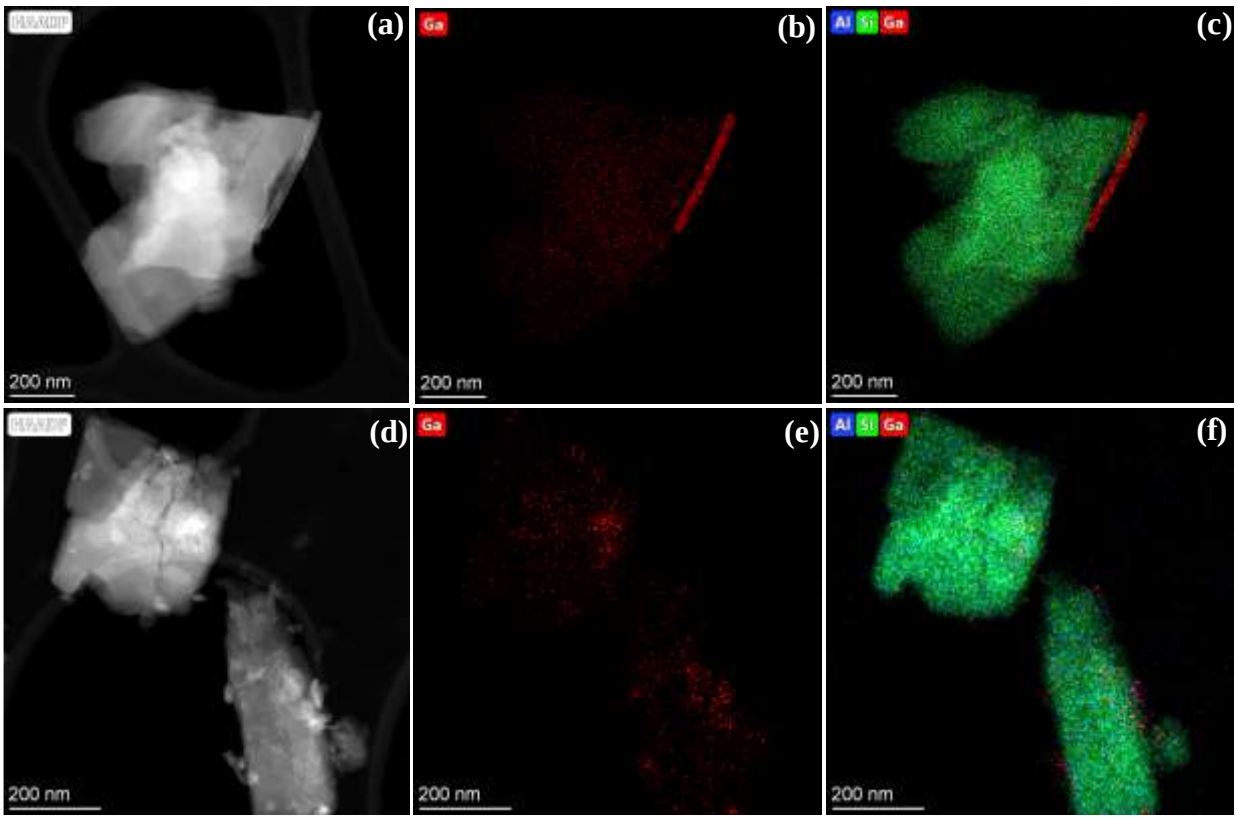


Figure S3: STEM images for Ga(5 wt.%)/ZSM-5 (a) support, (b) Ga distribution, and (c) overlaid Ga/Si/Al elemental mapping. STEM images for Ga(5 wt.%)/ZSM-$5_{0.8M}$ (d) support, (e) Ga distribution, and (f) overlaid Ga/Si/Al elemental mapping.

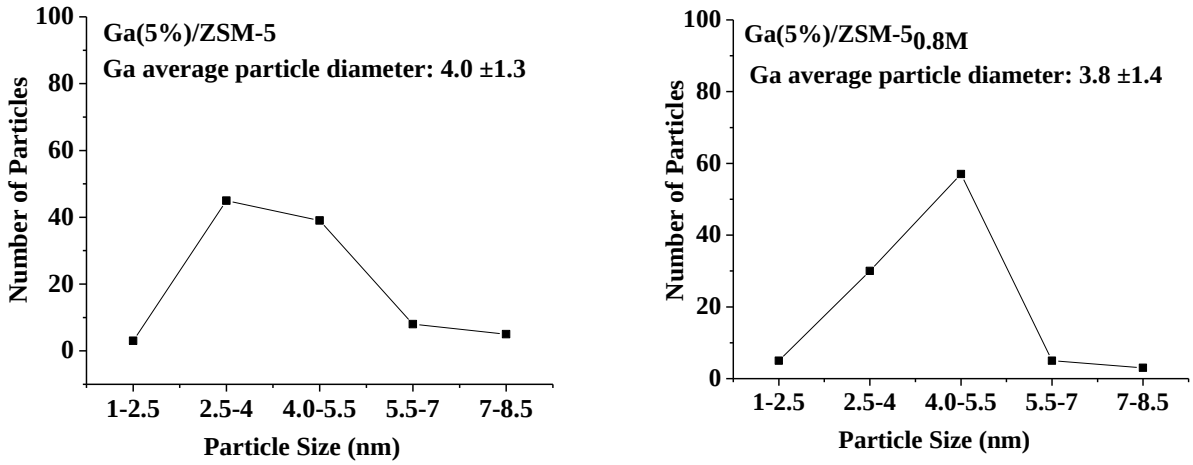


Figure S4: Ga average particle diameters in Ga(5 wt.%)/ZSM-5 and Ga(5 wt.%)/ZSM-$5_{0.8M}$.

Table S1: ICP-OES analysis for the liquid fraction collected after treating ZSM-5 with 0.2, 0.6, 0.8, & 1.0M NaOH

Modified-ZSM-5 Catalyst	**ICP-OES**				**Material loss (%)**
	Loss of SiO_2 (g)	Loss of Al_2O_3 (g)	Combined loss (g)	Loss of Si/Al	
0.2M	0.216	0.009	0.226	24	11.3±0.9
0.6M	0.665	0.051	0.716	13.0	20.6±1.1
0.8M	0.749	0.070	0.819	10.7	26.4±1.2
1.0M	0.788	0.103	0.891	7.7	38.6±3.1

Table S2: ICP-OES analysis for Ga (5 wt.%)/ZSM-$5_{0.8M}$ catalysts synthesized at different times.

Catalyst	Ga impregnation time	ICP-OES data of Ga nominal loading in wt.%
Ga (5 wt.%)/ZSM-$5_{0.8M}$	4	4.8
Ga (5 wt.%)/ZSM-$5_{0.8M}$	16	4.9
Ga (5 wt.%)/ZSM-$5_{0.8M}$	32	4.8

Table S3: XPS derived Si/Ga surface ratios of as-synthesized samples.

Sample	External surface Si/Ga ratio
[a]Ga(5 wt.%)/ZSM-$5_{0.8M}$	9
[b]Ga(5 wt.%)/ZSM-$5_{0.8M}$	13.5
[c]Ga(5 wt.%)/ZSM-$5_{0.8M}$	13.5
Ga(8 wt.%)/ZSM-$5_{0.8M}$	13
Ga(2 wt.%)/ZSM-$5_{0.8M}$	29

[a]Catalyst synthesis time of 4 hours, [b]catalyst synthesis time of 16 hours, and [c]catalyst synthesis time of 32 hours. External Si/Ga surface ratios were measured based on relative surface concentration of Ga, Na, Si, Al, and O atoms.

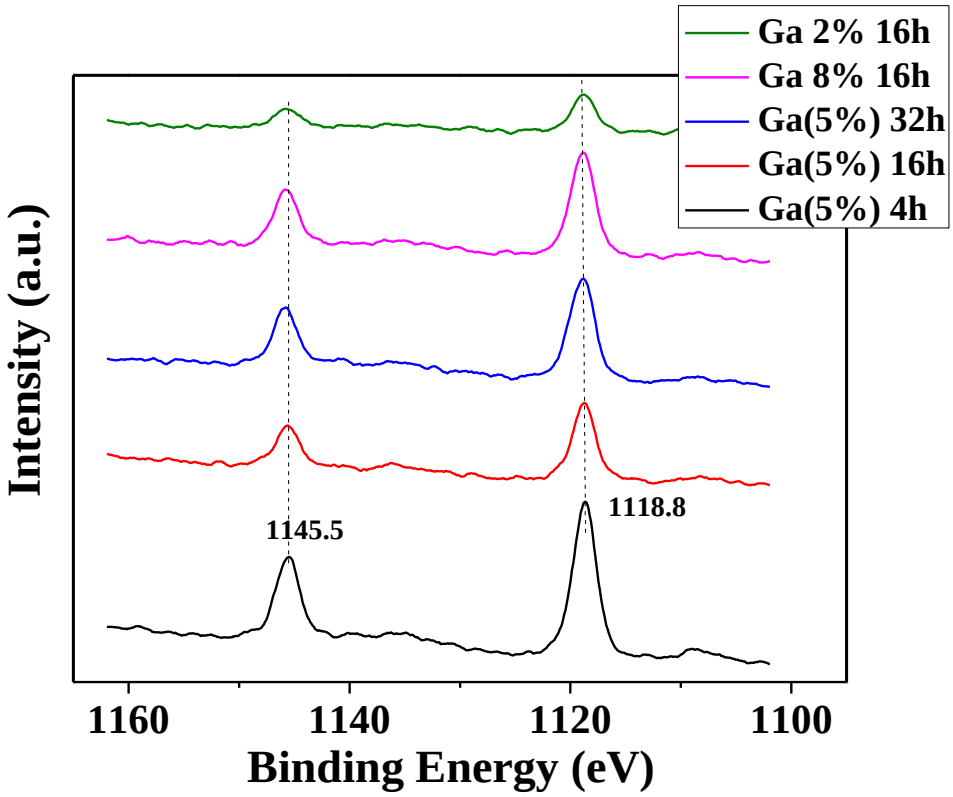


Figure S5: Ga 2p3/2 XPS spectra of 2, 5, and 8% gallium loadings for 4, 16 and 32 hours Ga wet-impregnation synthesis times.

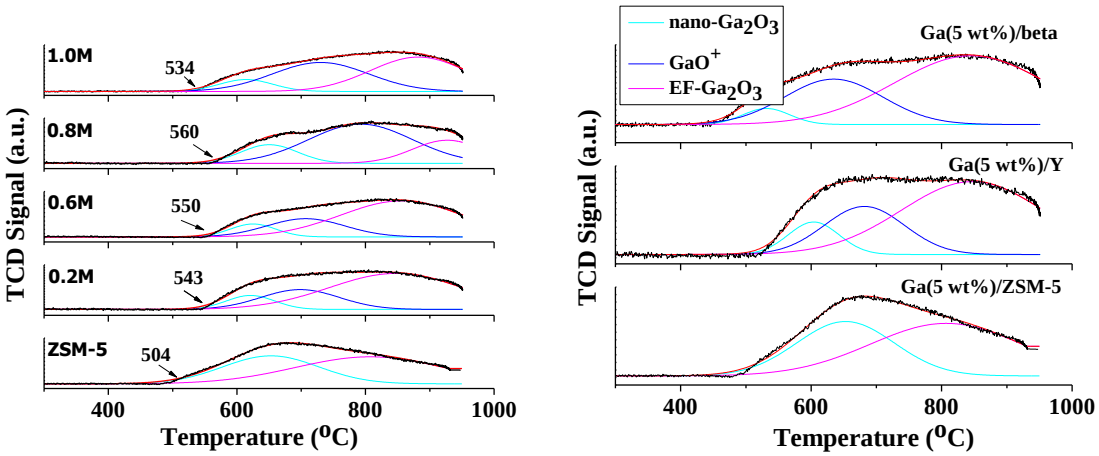


Figure S6: H_2-TPR profiles for Ga(5 wt.%)/ZSM-5 and Ga(5 wt.%)/ZSM-5_{xM} catalysts

Table S4: H_2-TPR composition data for each gallium oxide species (nano-Ga_2O_3, GaO^+, and EF-Ga_2O_3) quantified from their peak areas.			
Sample	% of Peak 1	% of Peak 2	% of Peak 3
Ga(5 wt.%)/ZSM-5	36.1	-	63.9
Ga(5 wt.%)/ZSM-$5_{0.2M}$	9.6	22.1	68.2
Ga(5 wt.%)/ZSM-$5_{0.6M}$	9.2	22.2	68.7
Ga(5 wt.%)/ZSM-$5_{0.8M}$	12.4	54.7	32.9
Ga(5 wt.%)/ZSM-$5_{1.0M}$	9.5	41.5	49.1
Ga(2 wt.%)/ZSM-$5_{1.0M}$	18.3	37.8	43.9
Ga(8 wt.%)/ZSM-$5_{1.0M}$	11.3	33.5	55.2
Ga(5 wt.%)/Beta	4.7	28.7	66.4
Ga(5 wt.%)/Y-zeolite	10.2	24.7	65.0

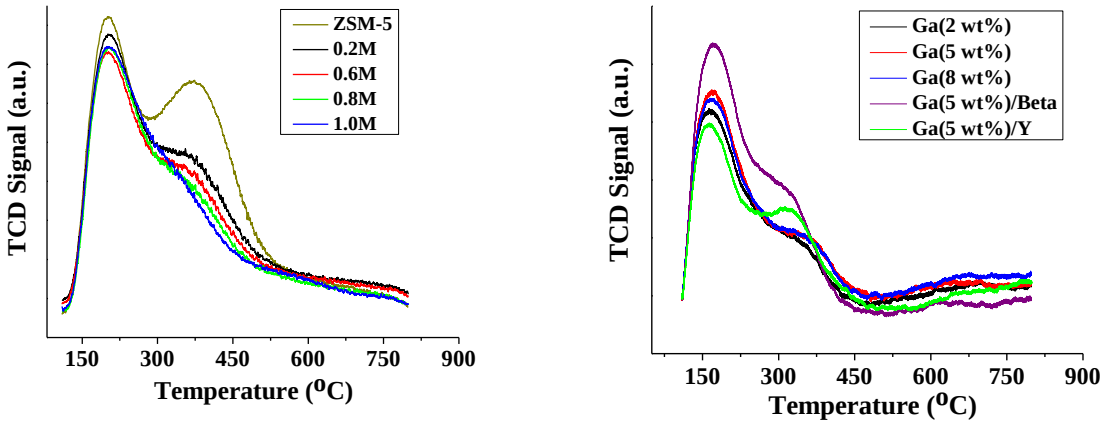


Figure S7: NH_3-TPD profiles of Ga(5 wt.%)/ZSM-5 and Ga(5 wt.%)/ZSM-5_{xM} (xM = 0.2, 0.6, 0.8 &1.0M).

NH3-Temperature Program Desorption (TPD) experiments: NH_3-TPD experiments were conducted with a Micrometrics AutoChem II 2090 chemisorption analyzer equipped with a Pfeiffer OmniStar quadrupole mass spectrometer. In a typical experiment, 0.4 g of the sample sample was taken in a U-shaped, flow-through, quartz sample tube. Prior analysis, sample was pretreated in He (50 ml/min; ramp rate 5°C/min) at 550 °C for 1 h. After cooling to 110°C, the catalyst was flushed with 50 ml/min Ar flow for one hour and then exposed to a flow of 100 ml/min 1%NH_3 in Ar for 1.5 hour. After purging with 50 ml/min Ar flow for 3.5 hour, TPD measurements were carried out in the range 110–800 °C at a heating rate of 10 °C/min. The amount of desorbed ammonia was determined based on the area under the peak.

NH_3-TPD: Figure S6 shows NH_3-temperature program desorption (TPD) data for Ga(5 wt.%)/ZSM-5 and Ga(5 wt.%)/ZSM-5_{xM} catalysts, with densities of acid sites calculated based on peak areas. Ga(5 wt.%)/ZSM-5 catalyst resulted two NH_3 desorption peaks that were centered at 200 °C and 373°C. The low temperature peak corresponds to weak acid sites that allowed NH_3 to desorb from extra framework silanol/alumina species, while the high temperature peak is attributed to strong acid sites that require more energy for NH_3 desorption from framework bridged hydroxyl groups (Si-OH-Al). Alkali treatment of ZSM-5 with 0.2M NaOH resulted in significant loss in intensity of the high temperature strong acid site peak while further increasing NaOH concentrations from 0.6M to 1.0M for ZSM-5 treatment exhibited a gradual loss of strong acid site peak intensities. A minimal loss in intensities of low temperature weak acid peaks (200 °C) were observed for modified Ga(5 wt.%)/ZSM-5_{xM} catalysts. The total density of acid sites dropped in the order of Ga(5 wt.%)/ZSM-5 (1.11 mmol/g) > Ga(5 wt.%)/ZSM-$5_{0.2M}$ (0.953 mmol/g) > Ga(5 wt.%)/ZSM-$5_{0.6M}$ (0.916 mmol/g) > Ga(5 wt.%)/ZSM-$5_{0.8M}$ (0.904 mmol/g) > Ga(5 wt.%)/ZSM-$5_{1.0M}$ (0.886 mmol/g). The loss of total acidity for used Ga/ZSM-5_{xM} catalysts could be due to loss of framework acid species (Si-OH-Al) and partial replacement of Bronsted acid sites (proton H^+ in hydroxyl group) by gallium cations. In addition, we conducted NH_3-TPD experiments for different Ga loadings on ZSM-$5_{0.8M}$ catalysts. However, no significant differences were measured

in corresponding weak and strong acid sites peak intensities for different Ga loadings on ZSM-$5_{0.8M}$ samples. These results suggest that changing the Ga loadings from 2 to 8 wt% on ZSM-$5_{0.8M}$ had a minimal effect on weak and strong acid sites. Also, application of NH_3-TPD to 5 wt% Ga loaded on beta and Y zeolites revealed two ammonia desorption peaks for both Ga(5 wt%)/beta and Ga(5 wt%)/Y zeolites at higher and lower temperatures which correspond to weak and strong acid sites, respectively, a result similar to that from application of NH_3-TPD to Ga(5 wt%)/ZSM-$5_{0.8M.}$ The peak intensities of corresponding weak acid sites for these three different catalysts increased in the order of Ga(5 wt%)/beta > Ga(5 wt%)/ZSM-$5_{0.8M}$ > Ga(5 wt%)/Y, and the peak intensities of the corresponding strong acid sites increased in the order Ga(5 wt%)/beta > Ga(5 wt%)/Y > Ga(5 wt%)/ZSM-$5_{0.8M}$. Activity data for these three catalysts showed that although ethanol liquid hydrocarbon yields were high (above 45%) for Ga(5 wt%)/ZSM-$5_{0.8M}$, they were virtually negligible for Ga(5 wt%)/beta and Ga(5 wt%)/Y formulations run at 350 °C and $0.4h^{-1}$ SV. These results suggest that pore structure plays a more crucial role in ethanol oligomerization than catalyst acidity.

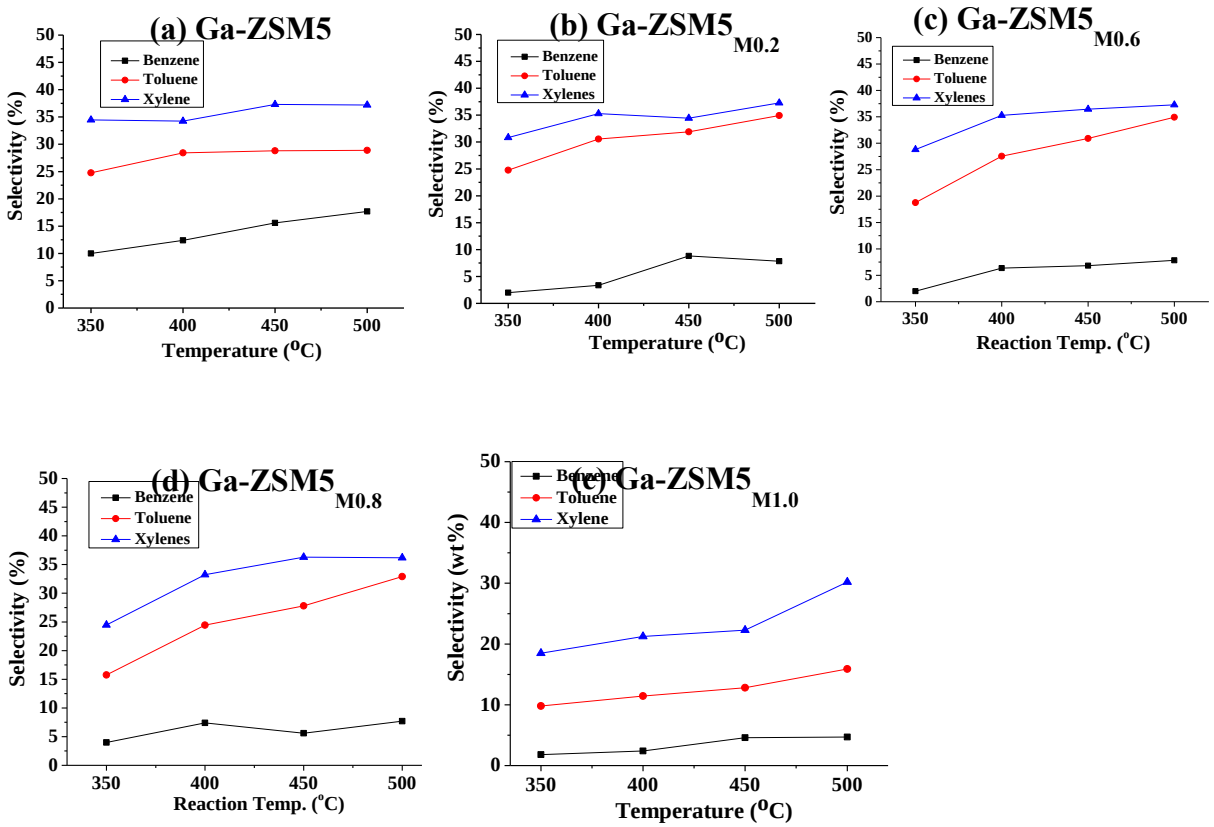
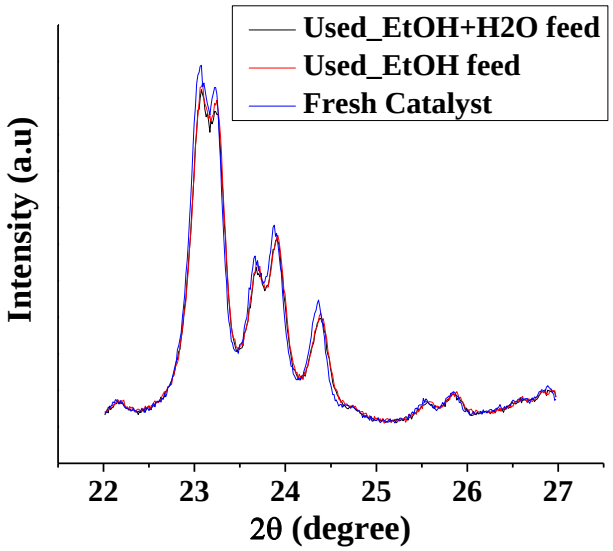


Figure S8: The effect of temperature on ethanol oligomerizations over Ga(5 wt.%)/ZSM-5 and Ga(5 wt.%)/ZSM-5_{xM} catalysts at 1.6h^{-1} WHSV

Ethanol was completely converted into hydrocarbons by all catalysts over a range of 350°C to 500°C. The liquid hydrocarbons contained C5-C6 aliphatic isomers, BTX, and C9-C10 aromatics. As shown in Figure S5, benzene, toluene, and xylene selectivity varied with reaction temperature, with higher temperatures increasing BTX selectivity whereas lower temperatures increased the fraction of C5-C6 paraffins. Based on these results, the parent Ga/ZSM-5 catalyst was more selective for BTX production compared to other catalysts, reaching a maximum of 84% BTX of the total liquids collected at 500 °C.



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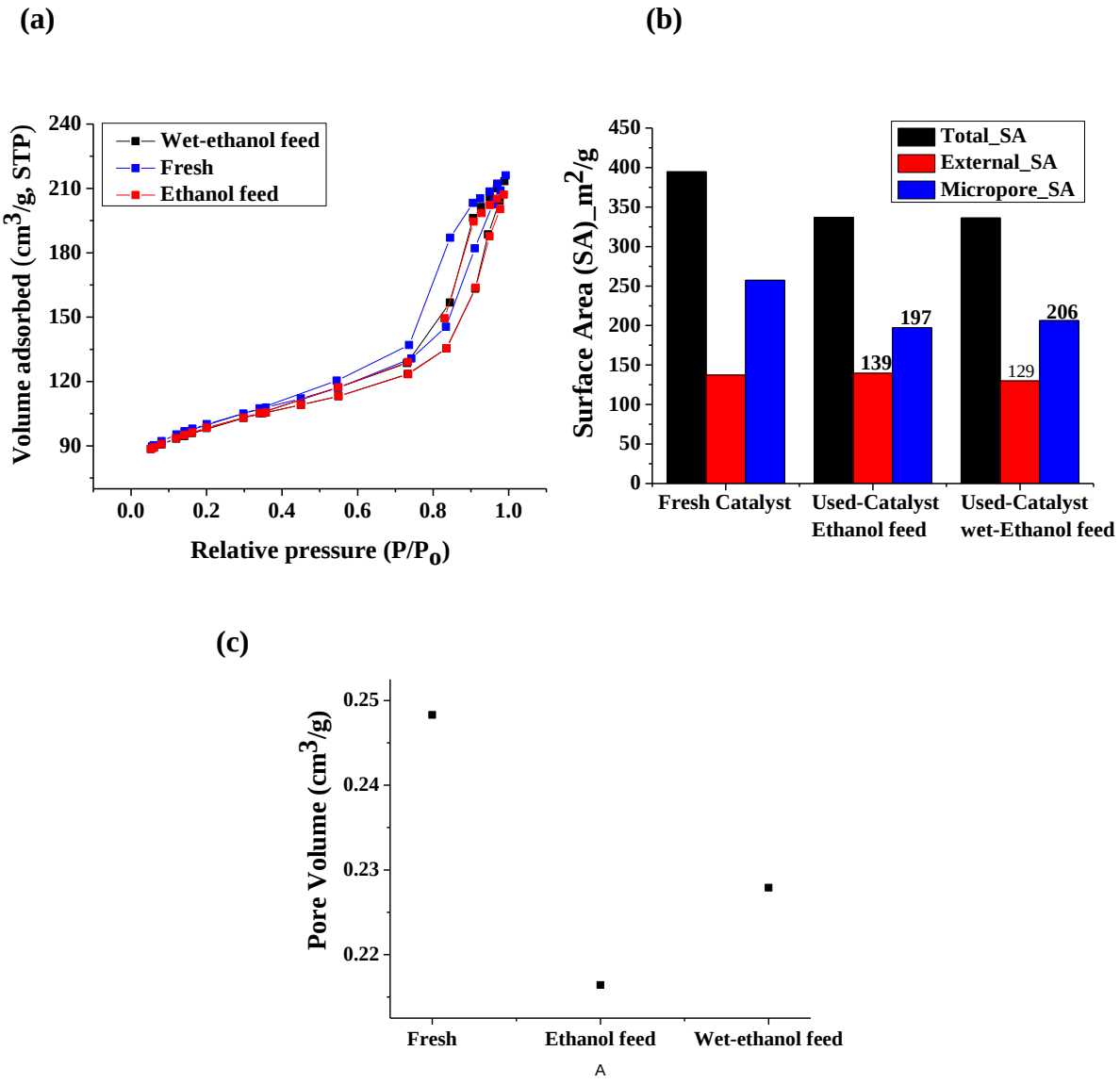

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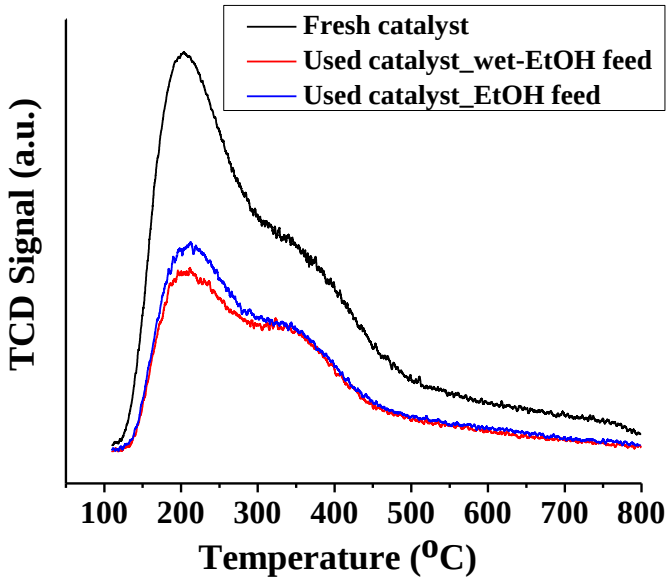
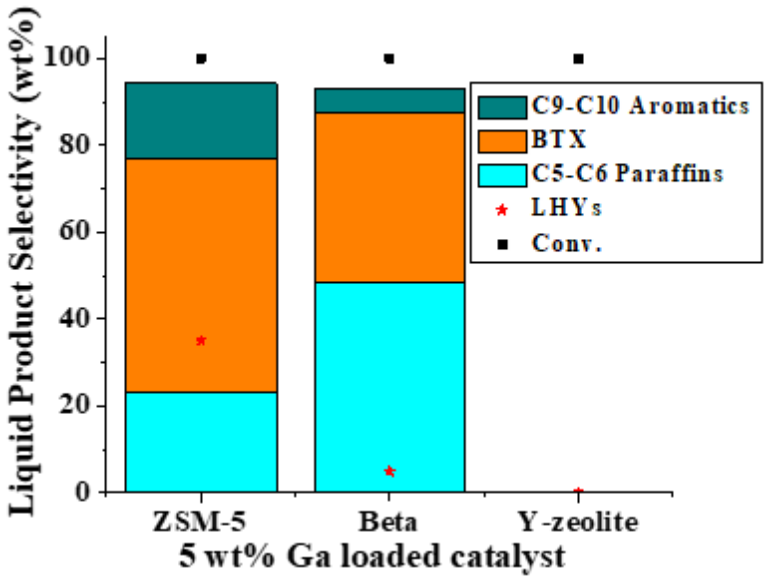


Figure S11: NH_3-TPD profiles of fresh catalyst and used catalysts for pure ethanol and wet ethanol.

NH_3-TPD experiments revealed that the total acidity of the used catalysts dropped to half that of fresh Ga(5 wt%)/ZSM-$5_{0.8M}$ catalyst due to loss of Bronsted acid sites by dealumination (alumina positioning as EFAl) and part replacement of Bronsted acid sites by gallium cations. The total acidity decreased in the order of fresh Ga/ZSM-$5_{0.8M}$ (0.904 mmol/g) > used Ga/ZSM-$5_{0.8M}$ for ethanol feed (0.461 mmol/g) > used Ga/ZSM-$5_{0.8M}$ for wet-ethanol feed (0.421 mmol/g). The loss in total acidity was higher for catalyst used for wet ethanol conversion that could be accounted by higher dealumination or replacement of Bronsted acid sites by gallium cations. These gallium cations can interact strongly with support zeolite via neighboring Bronsted acid sites, also known as docking points.



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