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

Supplementary information

Production of aromatics from butanol over Ga-promoted HZSM5 catalysts: Tuning of benzene-toluene-xylene and ethylbenzene (BTEX) selectivity

Tatinaidu Kella, Debaprasad Shee*

Department of Chemical Engineering, Indian Institute of Technology Hyderabad, Kandi – 502 284, Sangareddy, Telangana, India

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∗Corresponding author at: Department of Chemical Engineering, Indian Institute of Technology Hyderabad, Kandi 502284, Sangareddy, Telangana, India.

Tel.: +914023016210; fax: +914023016000.

E-mail address: dshee@che.iith.ac.in (Dr. Debaprasad Shee)

Table S1 Reproducibility of experimental runs over 5Ga-HZSM5 catalysts for the conversion of butanol to aromatics.

	Selectivity, %[a]						
	C_1-C_2	**C_3-C_4**	**C_5-C_{12}**	**Aromatics**	**BTEX**	**Higher aromatics**	**Carbon balance (% error)**
Run 1	2.55	51.97	0.53	44.86	37.79	7.07	4.53
Run 2	2.63	53.76	0.55	43.07	36.59	6.47	5.26
Run 3	2.50	51.95	0.56	44.99	38.04	6.95	5.18

[a]Reaction conditions: Temperature = 673 K; WHSV = 0.75 h^{-1}; Pressure = 1 bar.

	Selectivity, %[b]						
	C_1-C_2	**C_3-C_4**	**C_5-C_{12}**	**Aromatics**	**BTEX**	**Higher aromatics**	**Carbon balance (% error)**
Run 4	27.48	13.02	0.09	58.05	43.00	15.05	34.85
Run 5	33.08	11.47	0.05	53.85	41.30	12.55	32.15

[b]Reaction conditions: Temperature = 823 K; WHSV = 0.75 h^{-1}; Pressure = 20 bar.

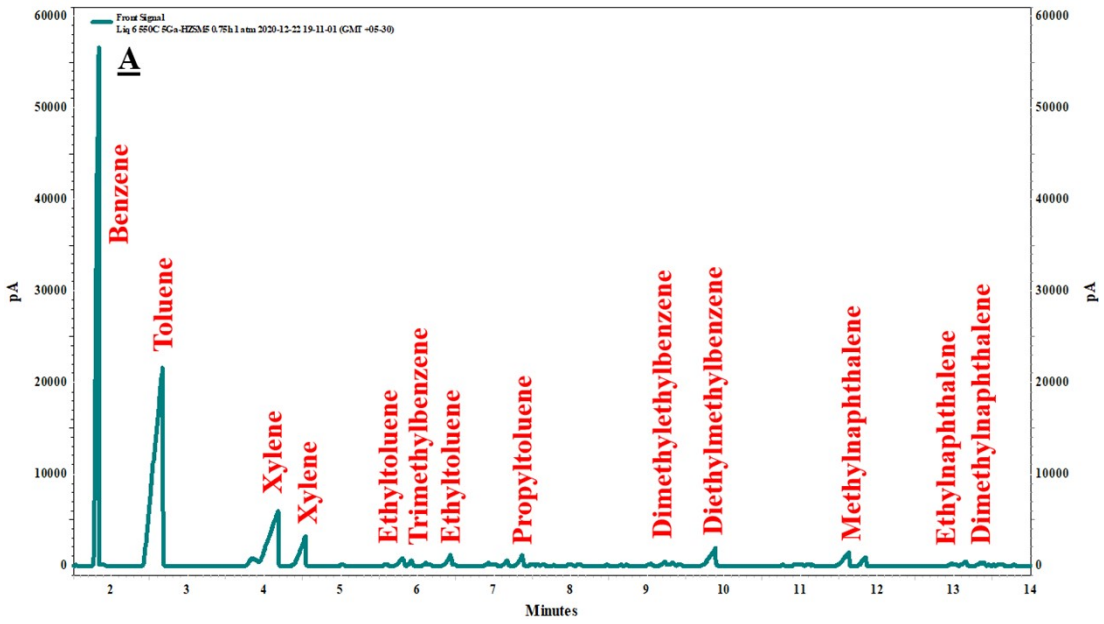
Table S2 Selectivity of C_9-C_{13} aromatics over 5Ga-HZSM5 catalyst for the conversion of butanol to aromatics, Reaction conditions: Temperature = 823 K; WHSV = 0.75 h^{-1}.

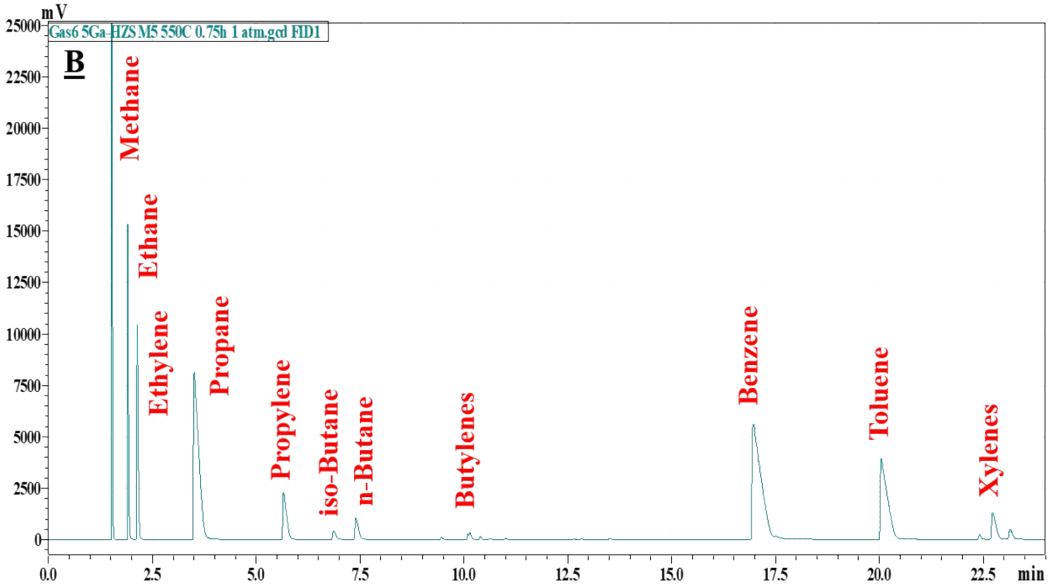
	Selectivity, %						
Reaction Pressure (bar)	**C_9**	**C_{10}**	**C_{11}**	**C_{12}**	**C_{13}**	**Total Higher aromatics**	**Carbon balance (% error)**
1	1.58	2.79	1.48	1.09	0.13	7.07	4.53
5	2.86	3.46	3.25	1.03	0.37	10.96	8.41
10	3.06	4.01	3.65	1.15	0.78	12.65	11.52
20	3.74	4.71	4.58	1.55	0.47	15.05	34.85
30	3.69	5.37	5.11	1.62	0.57	16.36	47.08

Catalyst	**SA_{BET} [a] (m^2/g)**	**A_E [b] (m^2/g)**	**V_T [c] (cm^3/g)**	**V_m [d] ($cm.^3/g$)**	**A_m [e] (m^2/g)**
Fresh 5Ga-HZSM5	350	143	0.25	0.10	207
5Ga-HZSM5_1 bar	282	155	0.23	0.06	127
5Ga-HZSM5_5 bar	270	125	0.23	0.07	145
5Ga-HZSM5_10 bar	258	112	0.22	0.07	146
5Ga-HZSM5_20 bar	281	172	0.22	0.06	108
5Ga-HZSM5_30 bar	239	79	0.20	0.08	159

Table S3 Textural properties of spent 5Ga-HZSM5 catalysts.

[a]BET surface area, [b]external surface area derived from t-Plot method, [c]total pore volume derived from BJH method, [d]micropore volume derived from t-Plot method, [e]micropore surface area derived from t-Plot method


Front Signal
Liq 6 550C 5Ga-HZSM5 0.75h 1 atm 2020-12-22 19-11-01 (GMT -05:30)
A
Benzene
Toluene
Xylene
Xylene
Ethyltoluene
Trimethylbenzene
Ethyltoluene
Propyltoluene
Dimethylethylbenzene
Diethylmethylbenzene
Methylnaphthalene
Ethylnaphthalene
Dimethylnaphthalene
pA
Minutes


mV
Gas6 5Ga-HZSM5 550C 0.75h 1 atm.gcd FID1
B
Methane
Ethane
Ethylene
Propane
Propylene
iso-Butane
n-Butane
Butylenes
Benzene
Toluene
Xylenes
min

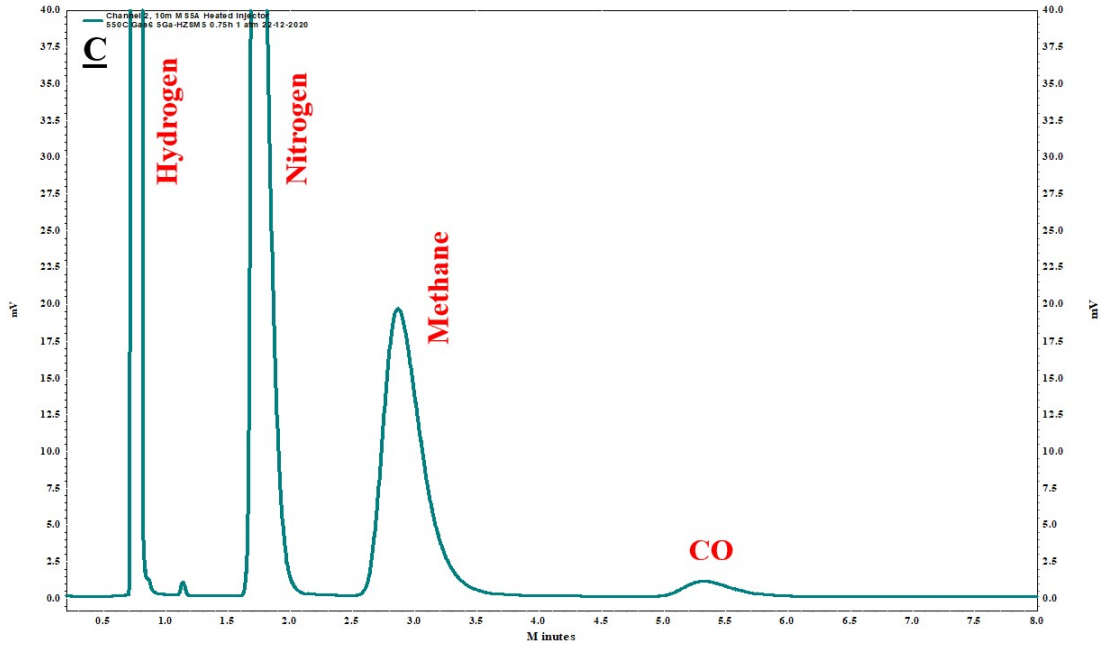


Fig. S1 GC chromatograms for A) liquid sample analysis by FID, B) gas sample analysis by FID, C) permanent gas analysis by TCD. Reaction conditions: Temperature = 823 K; WHSV = 0.75 h^{-1}; Pressure = 1 atm, 5Ga-HZSM5 catalyst.

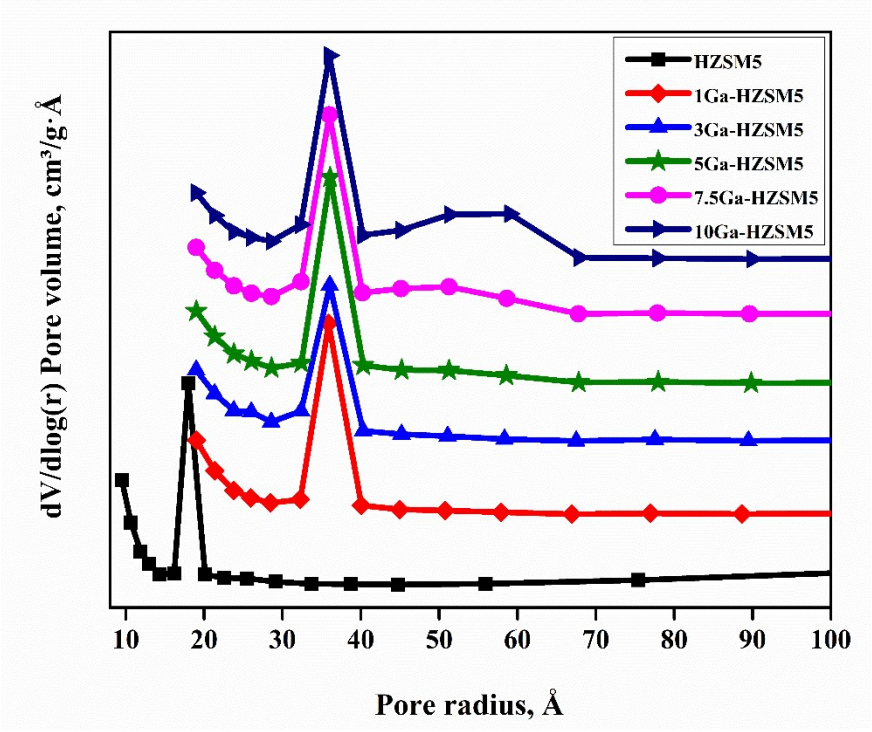


Fig. S2 Pore size distribution of xGa-HZSM5 (x = 0 to 10 wt%) catalysts.

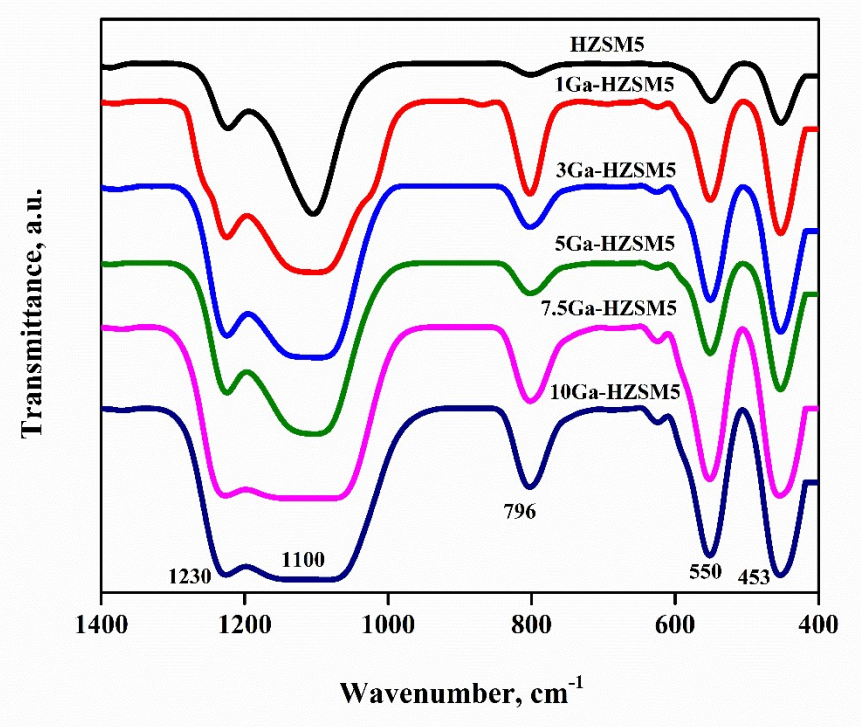


Fig. S3 FTIR spectra of xGa-HZSM5 (x = 0 to 10 wt%) catalysts.

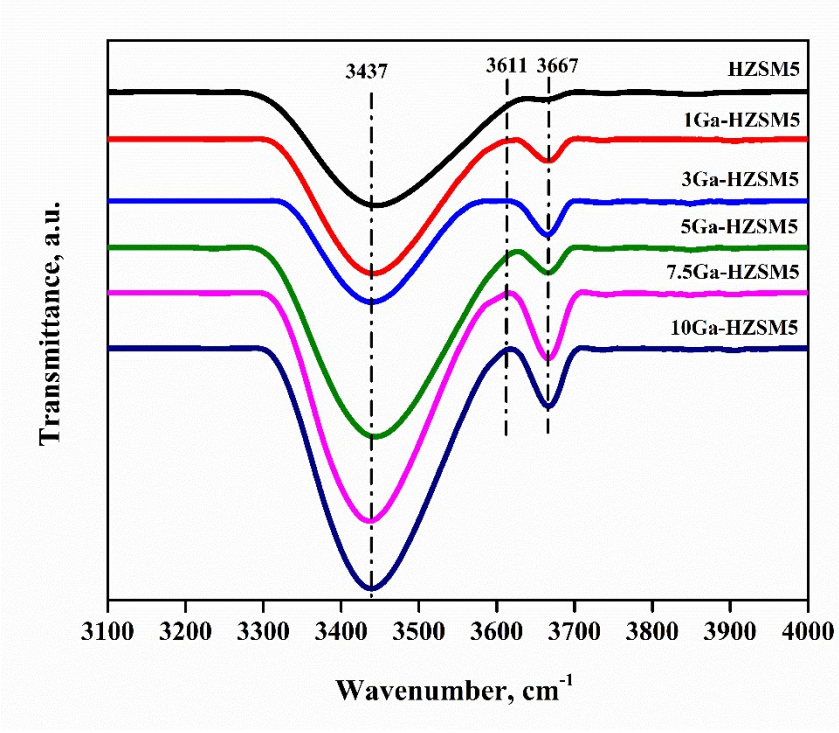


Fig. S4 FTIR spectra of xGa-HZSM5 (x = 0 to 10 wt%) catalysts in the hydroxyl region.

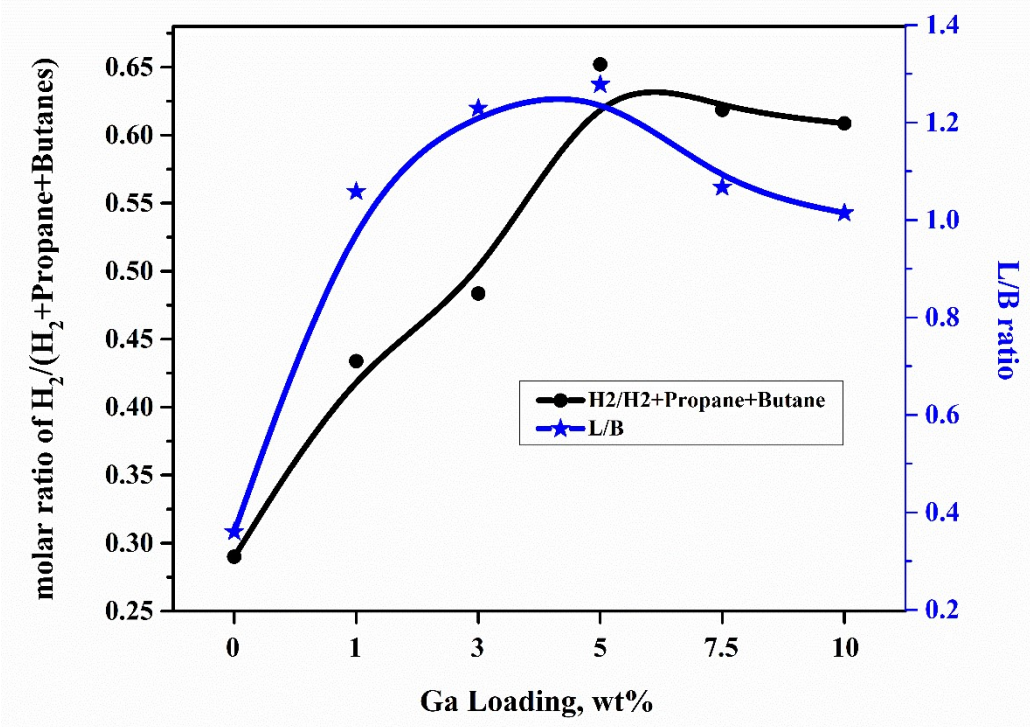


Fig. S5 Molar ratios of H_2/(H_2+Propane+Butanes) and L/B ratio as a function of Ga loading, Reaction conditions: Temperature = 673 K; WHSV = 0.75 h^{-1}; Pressure = 1 atm.

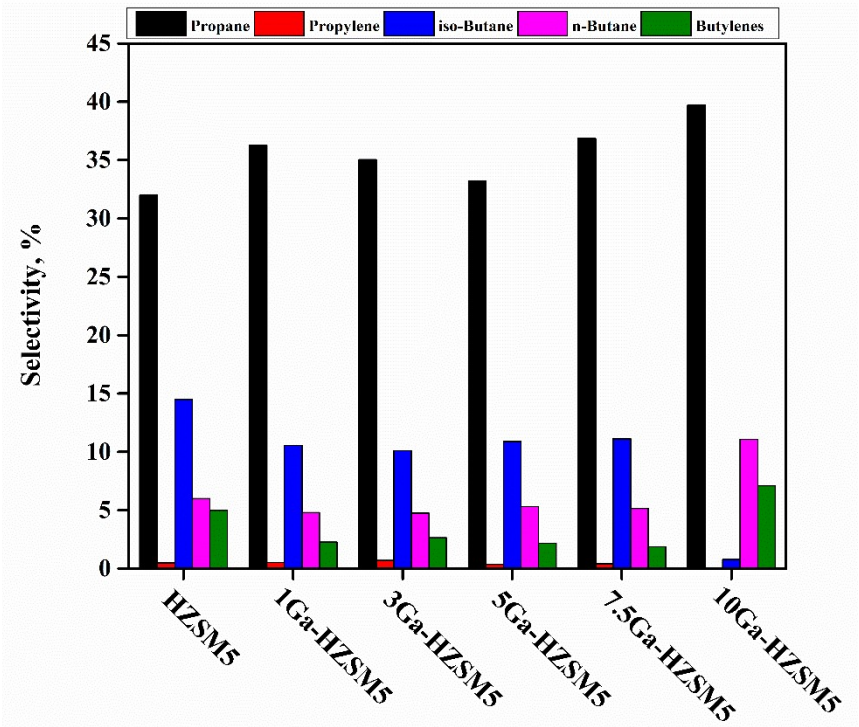


Fig. S6 Effect of Ga loading on selectivity of C_3 - C_4 hydrocarbons, Reaction conditions: Temperature = 673 K; WHSV = 0.75 h^{-1}; Pressure = 1 atm.

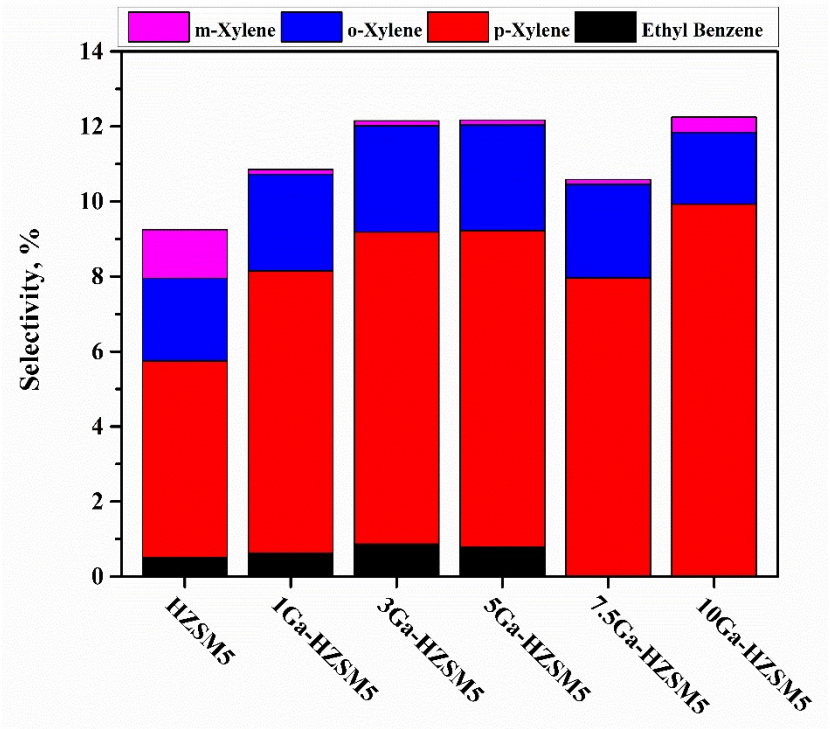


Fig. S7 Effect of Ga loading on selectivity of C_8 hydrocarbons, Reaction conditions: Temperature = 673 K; WHSV = 0.75 h^{-1}; Pressure = 1 atm.

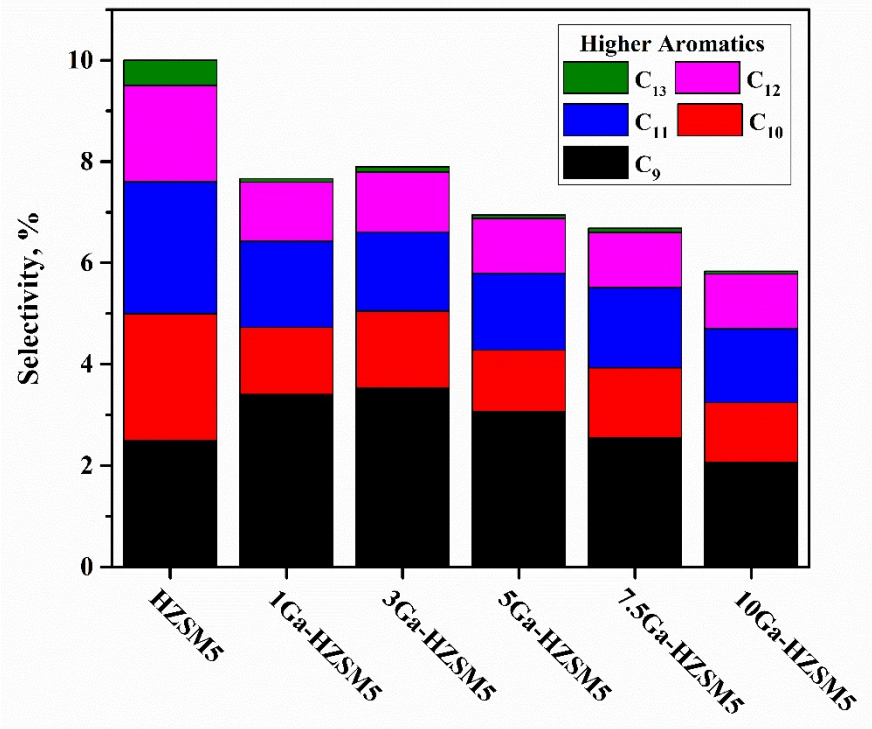


Fig. S8 Effect of Ga loading on selectivity of higher aromatics, Reaction conditions: Temperature = 673 K; WHSV = 0.75 h^{-1}; Pressure = 1 atm.

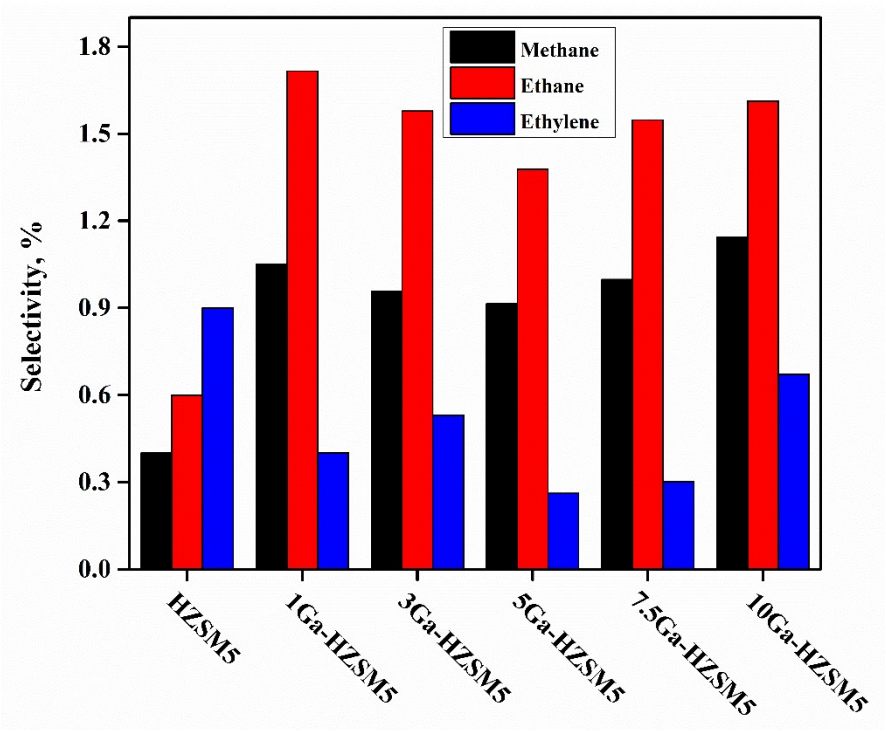


Fig. S9 Effect of Ga loading on selectivity of C_1 - C_2 hydrocarbons, Reaction conditions: Temperature = 673 K; WHSV = 0.75 h^{-1}; Pressure = 1 atm.

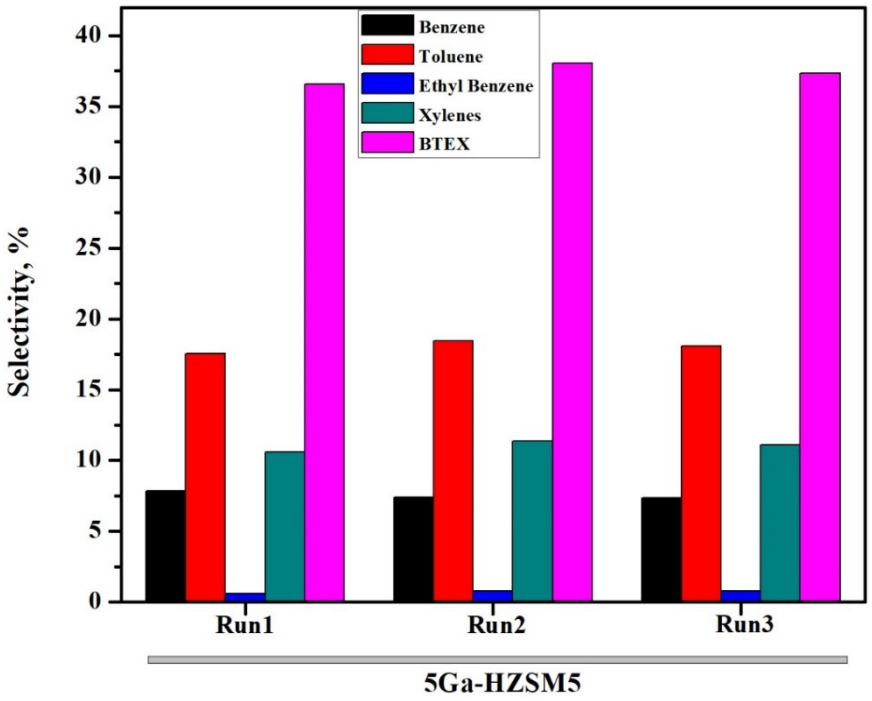


Fig. S10 Reproducibility of BTEX hydrocarbons, Reaction conditions: Temperature = 673 K; WHSV = 0.75 h^{-1}; Pressure = 1 atm; 5Ga-HZSM5 catalyst.

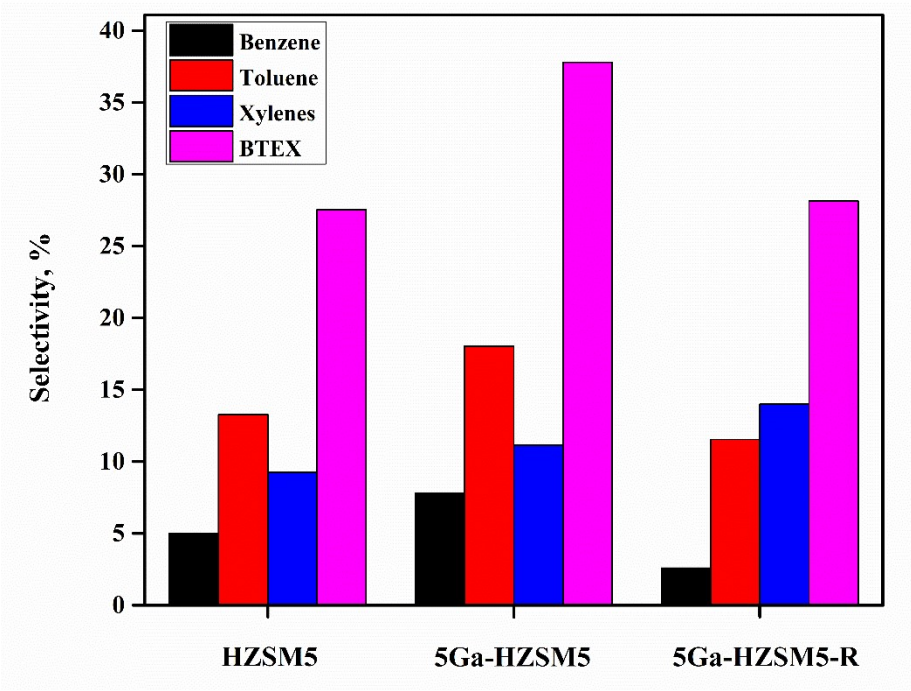


Fig. S11 Selectivity for BTEX hydrocarbons over HZSM5, 5Ga-HZSM5, and reduced 5Ga-HZSM5 catalysts, Reaction conditions: Temperature = 673 K; WHSV = 0.75 h^{-1}; Pressure = 1 atm.

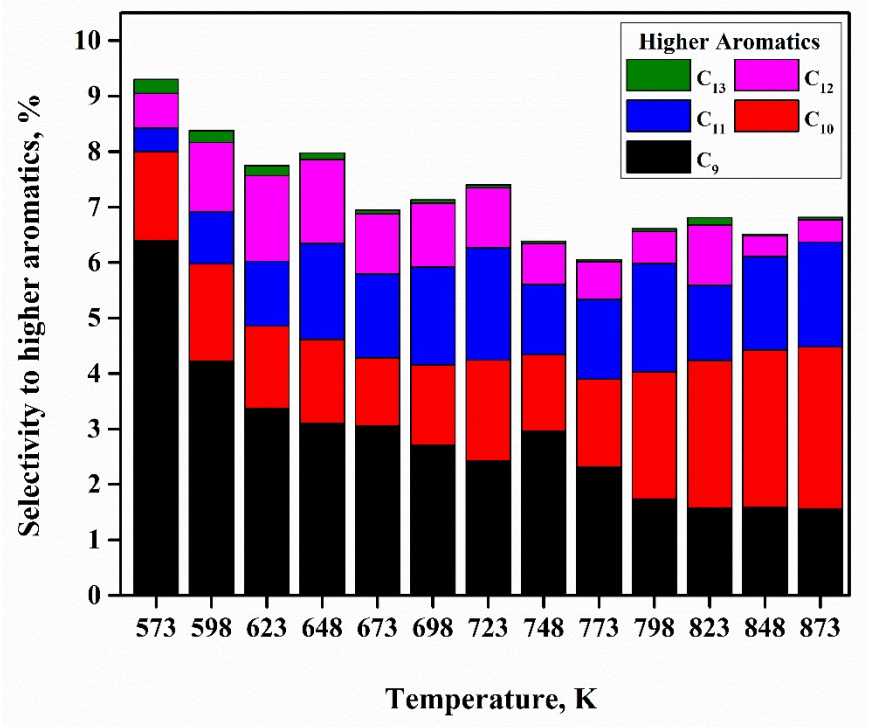


Fig. S12 Effect of temperature on the selectivity of higher aromatics, Reaction conditions: WHSV = 0.75 h^{-1}; Pressure = 1 atm; 5Ga-HZSM5 catalyst.

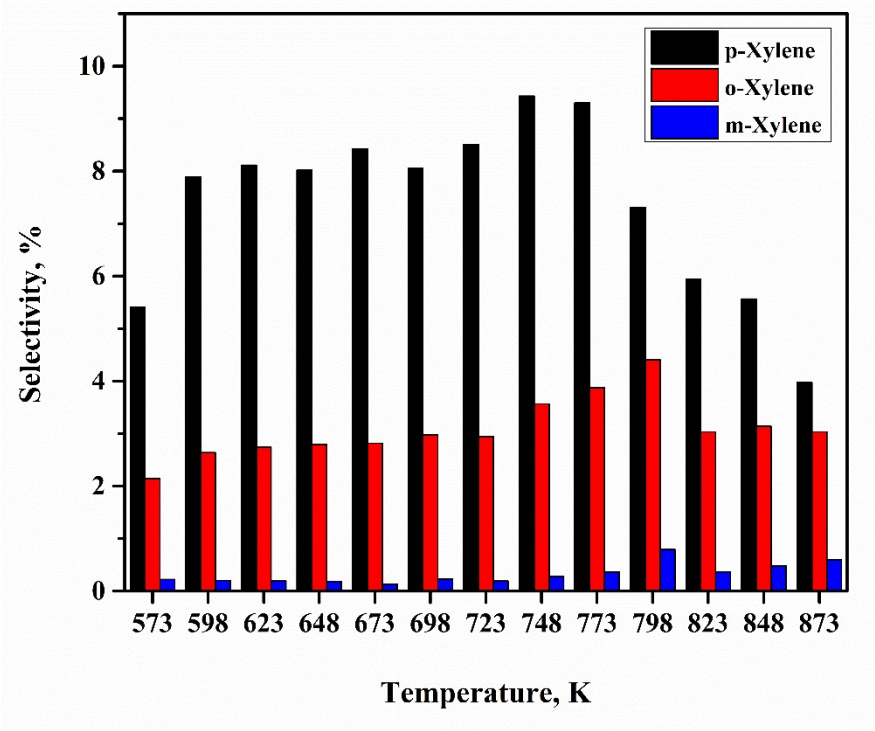


Fig. S13 Effect of temperature on selectivity of xylene isomers, Reaction conditions: WHSV = 0.75 h^{-1}; Pressure = 1 atm; 5Ga-HZSM5 catalyst.

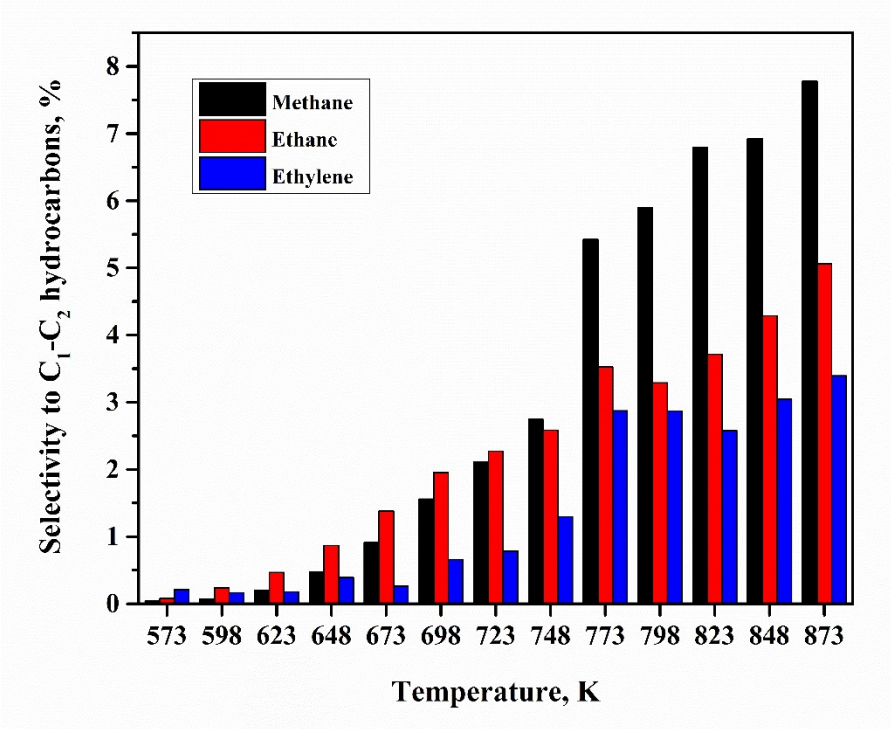


Fig. S14 Effect of temperature on selectivity of C_1 - C_2 hydrocarbons, Reaction conditions: WHSV = 0.75 h^{-1}; Pressure = 1 atm; 5Ga-HZSM5 catalyst.

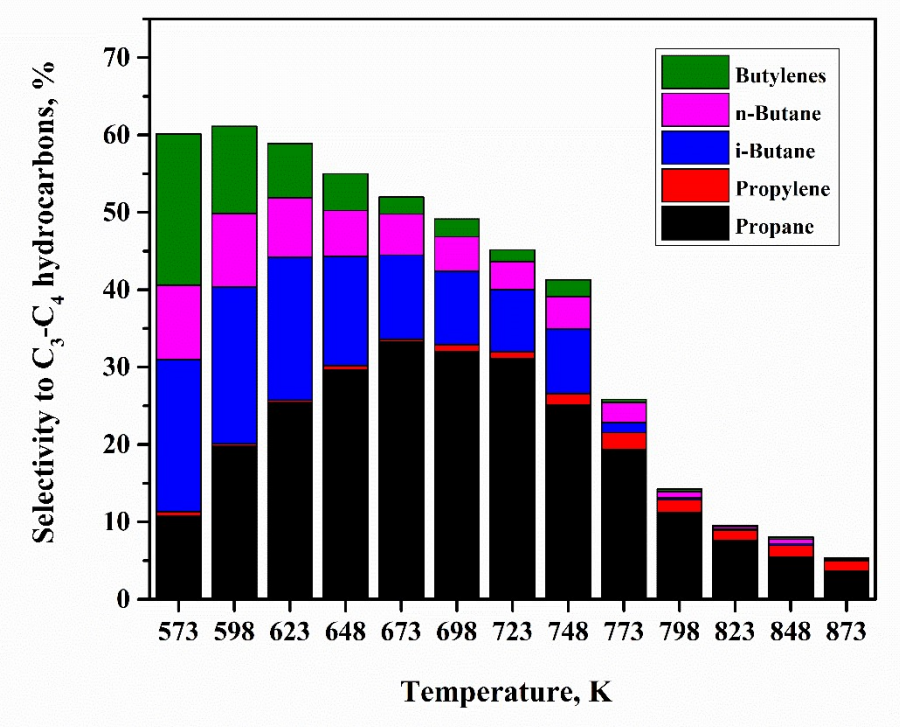


Fig. S15 Effect of temperature on selectivity of C_3 - C_4 hydrocarbons, Reaction conditions: WHSV = 0.75 h^{-1}; Pressure = 1 atm; 5Ga-HZSM5 catalyst.

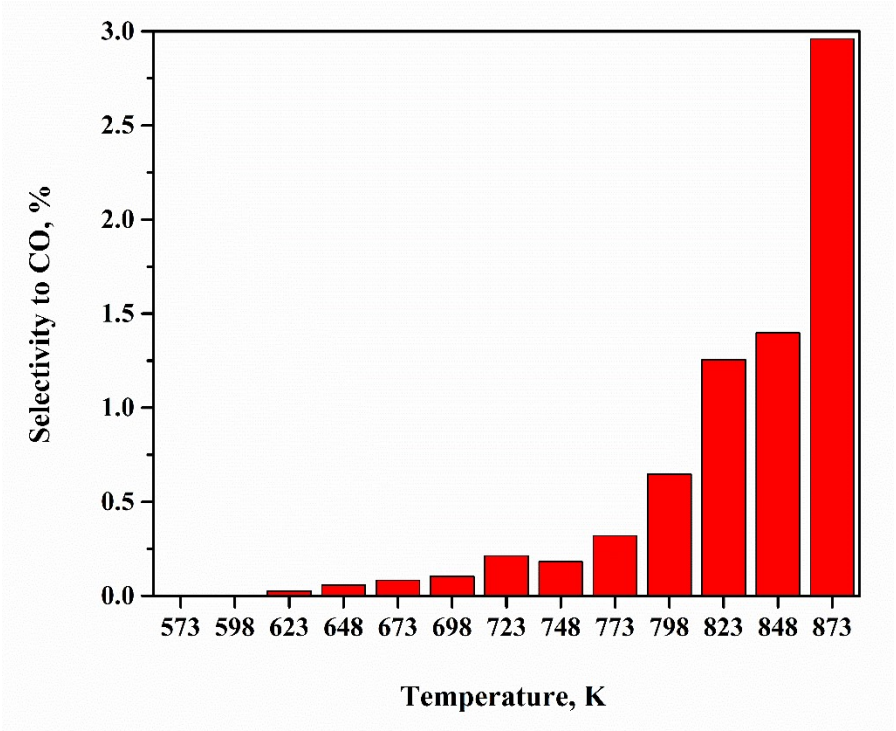


Fig. S16 Effect of temperature on the selectivity of CO, Reaction conditions: WHSV = 0.75 h^{-1}; Pressure = 1 atm; 5Ga-HZSM5 catalyst.

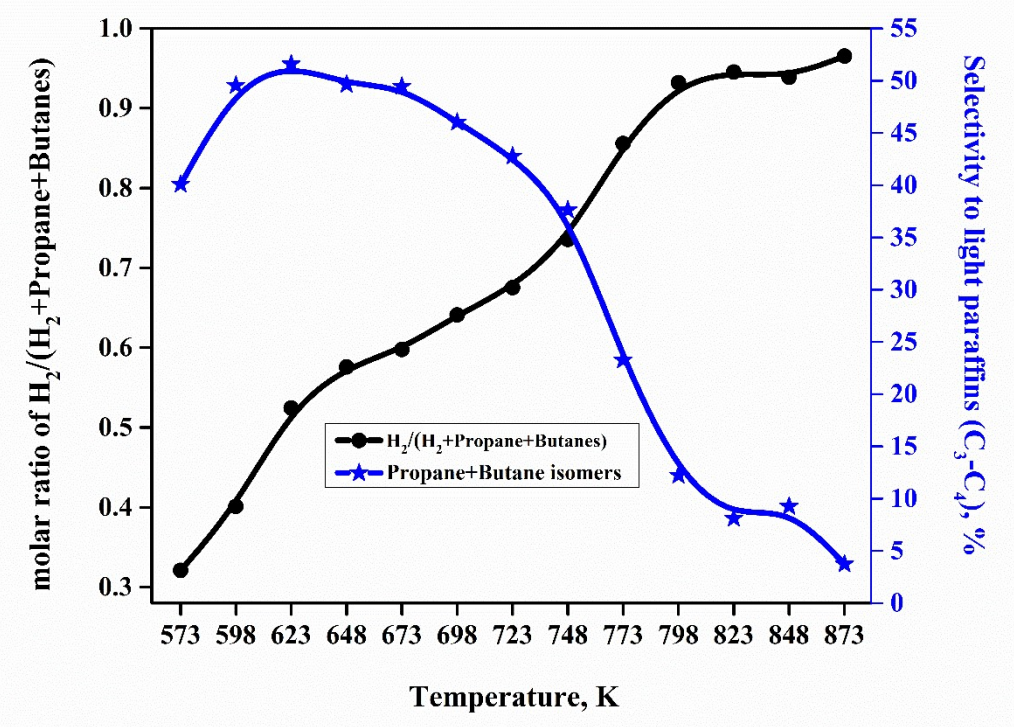


Fig. S17 Effect of temperature on molar ratios of H_2/(H_2+Propane+Butanes) and C_3-C_4 paraffins, Reaction conditions: WHSV = 0.75 h^{-1}; Pressure = 1 atm; 5Ga-HZSM5 catalyst.

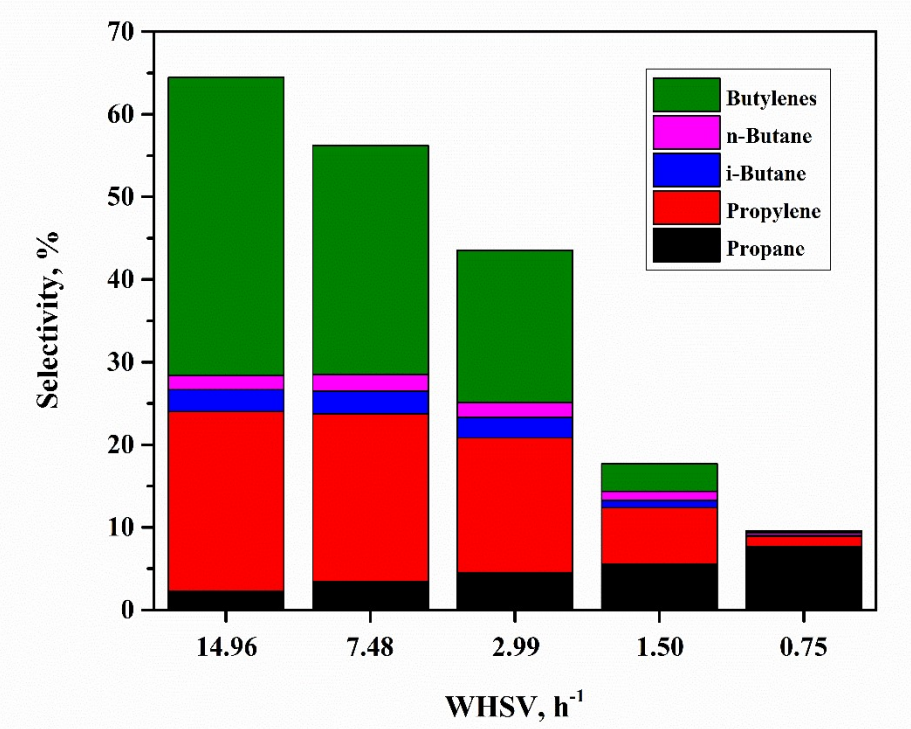


Fig. S18 Effect of WHSV on selectivity of C_3-C_4 hydrocarbons, Reaction conditions: Temperature = 823 K; Pressure = 1 atm; 5Ga-HZSM5 catalyst.

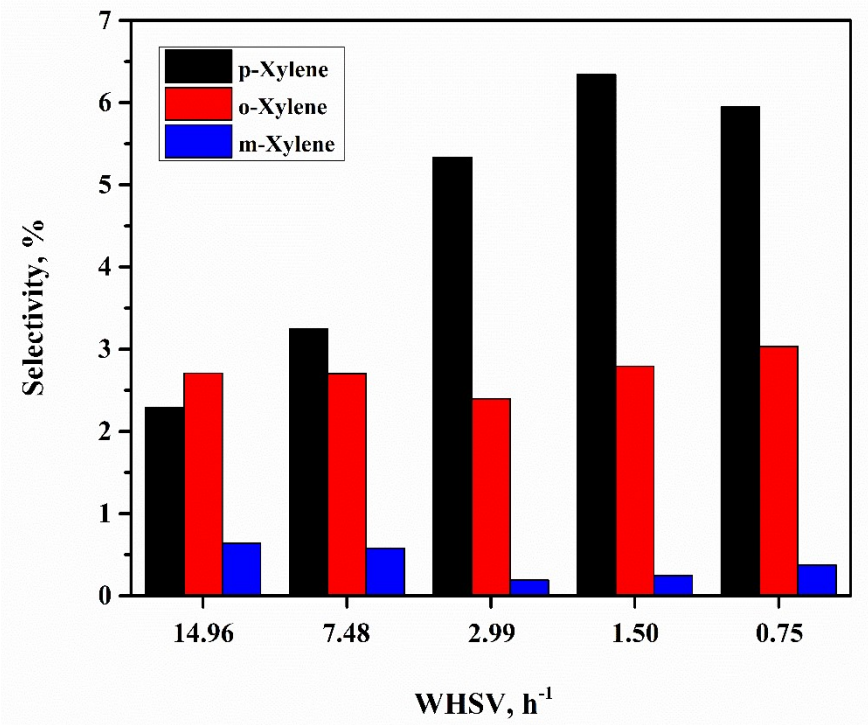


Fig. S19 Effect of WHSV on selectivity of xylene isomers, Reaction conditions: Temperature = 823 K; Pressure = 1 atm; 5Ga-HZSM5 catalyst.

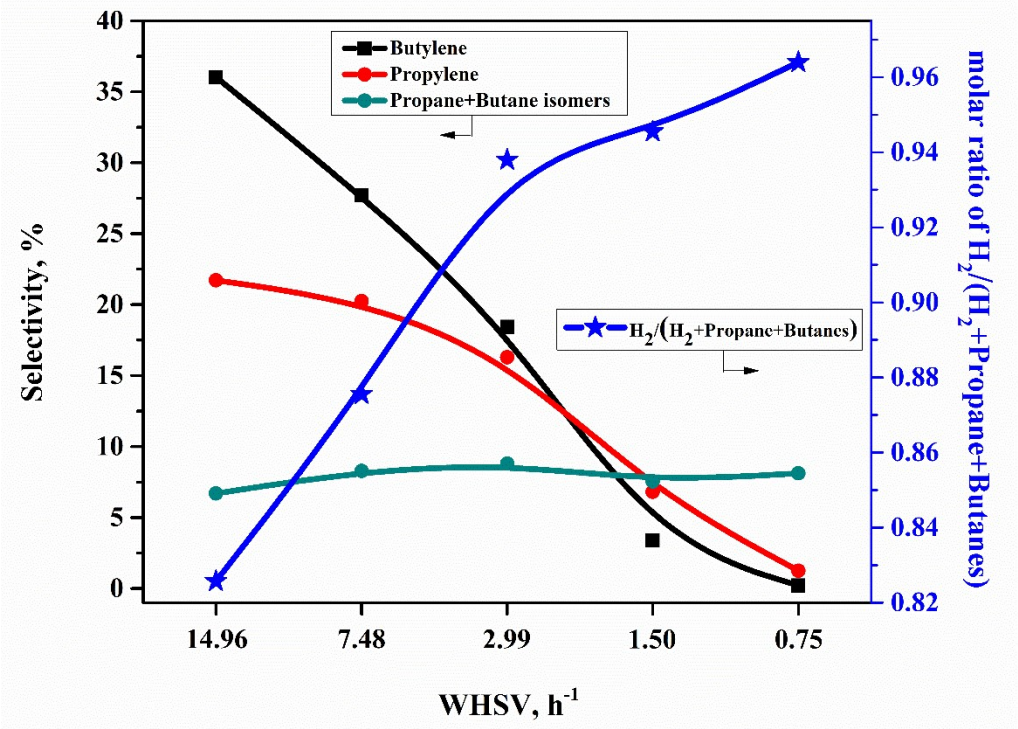


Fig. S20 Effect of WHSV on molar ratios of H_2/(H_2+Propane+Butanes) and C_3-C_4 hydrocarbons selectivity, Reaction conditions: Temperature = 823 K; Pressure = 1 atm; 5Ga-HZSM5 catalyst.

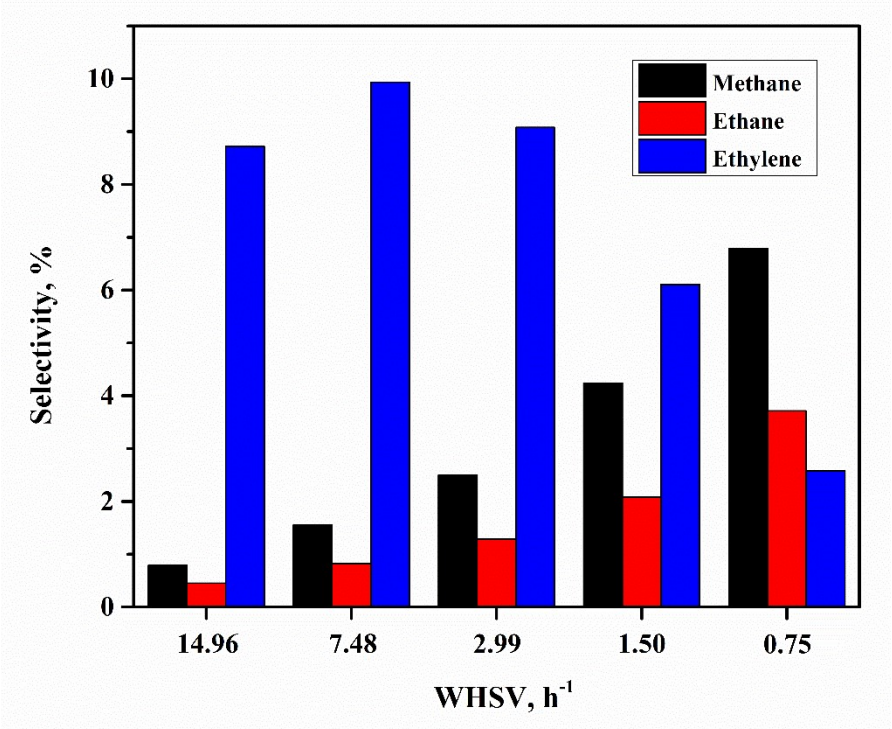


Fig. S21 Effect of WHSV on selectivity of C_1-C_2 hydrocarbons, Reaction conditions: Temperature = 823 K; Pressure = 1 atm; 5Ga-HZSM5 catalyst.

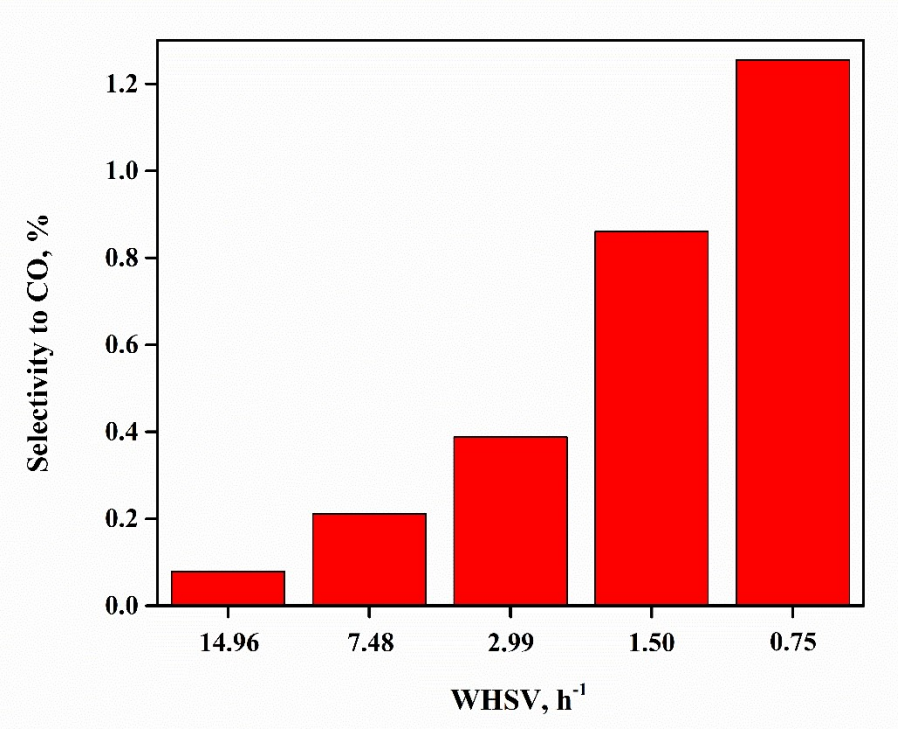


Fig. S22 Effect of WHSV on selectivity of CO, Reaction conditions: Temperature = 823 K; Pressure = 1 atm; 5Ga-HZSM5 catalyst.

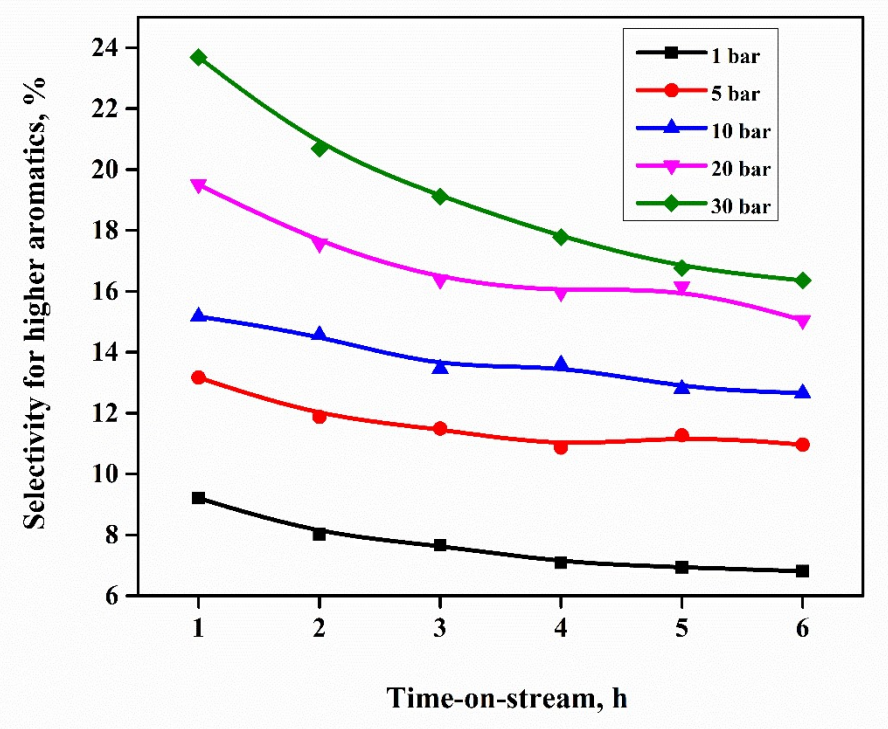


Fig. S23 Effect of pressure on higher aromatics selectivity over 6 h TOS, Reaction conditions: Temperature = 823 K; WHSV = 0.75 h^{-1}; 5Ga-HZSM5 catalyst.

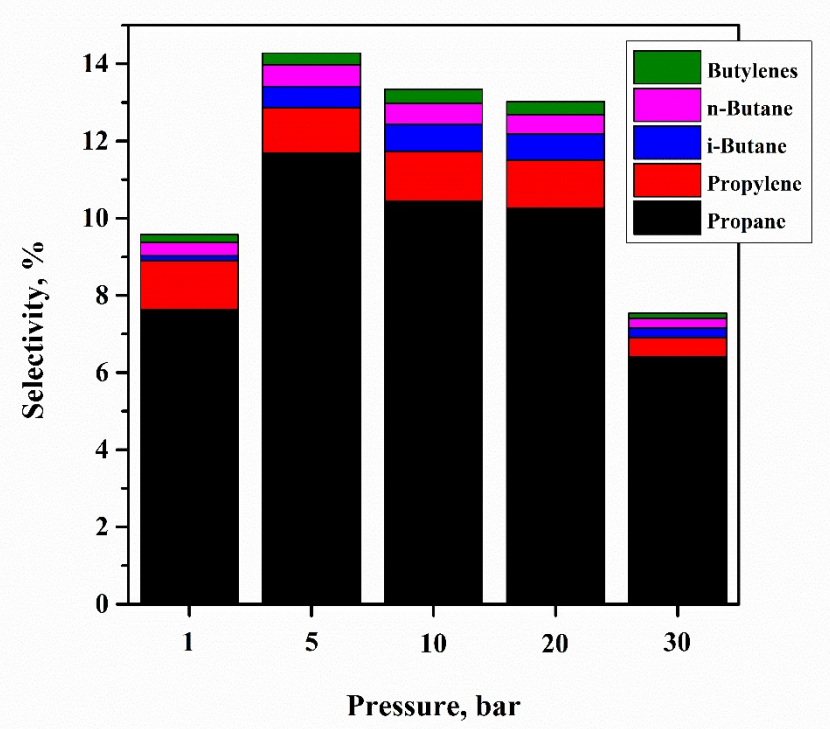


Fig. S24 Effect of pressure on selectivity of C_3-C_4 hydrocarbons, Reaction conditions: Temperature = 823 K; WHSV = 0.75 h^{-1}; 5Ga-HZSM5 catalyst.

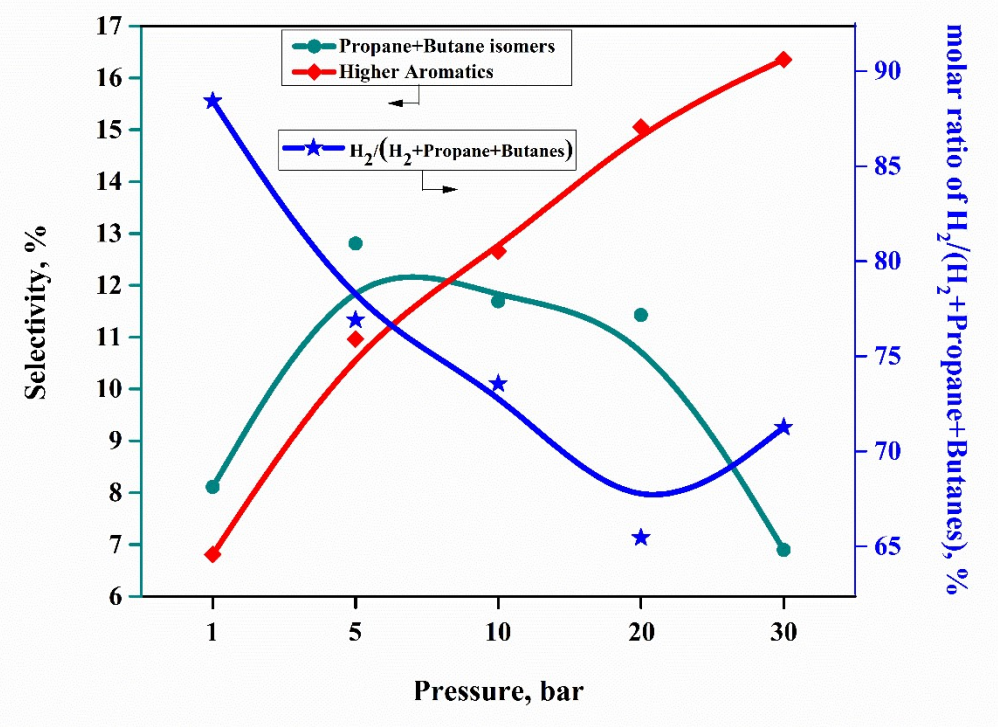


Fig. S25 Effect of pressure on molar ratios of $H_2/(H_2+Propane+Butanes)$ and C_3-C_4 paraffins selectivity, Reaction conditions: Temperature = 823 K; WHSV = 0.75 h^{-1}; 5Ga-HZSM5 catalyst.

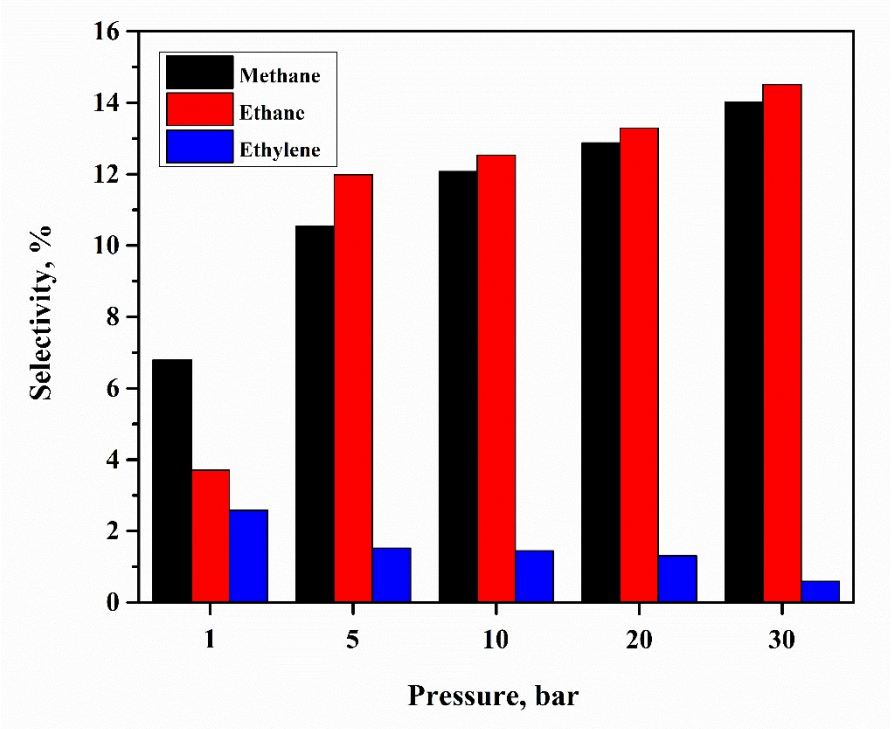


Fig. S26 Effect of pressure on selectivity of C_1-C_2 hydrocarbons, Reaction conditions: Temperature = 823 K; WHSV = 0.75 h^{-1}; 5Ga-HZSM5 catalyst.

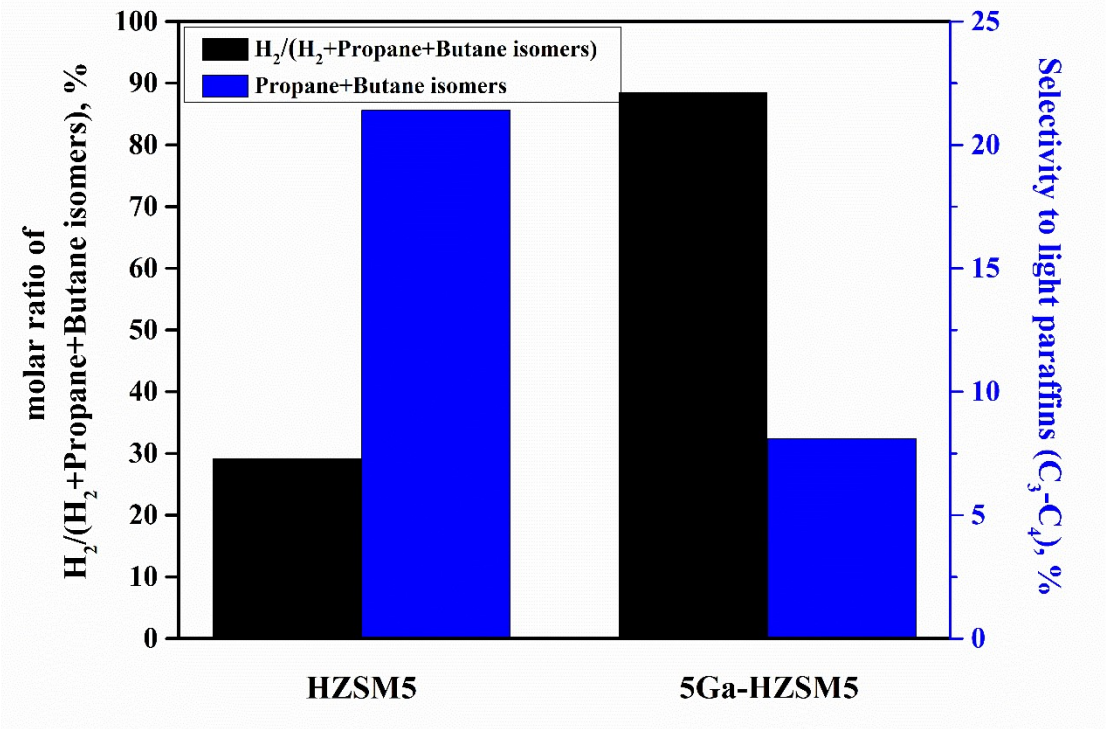


Fig. S27 Molar ratios of $H_2/(H_2+Propane+Butanes)$ and C_3-C_4 paraffins selectivity over HZSM5 and 5Ga-HZSM5 catalyst, Reaction conditions: Temperature = 823 K; WHSV = 0.75 h^{-1}; Pressure = 1atm.

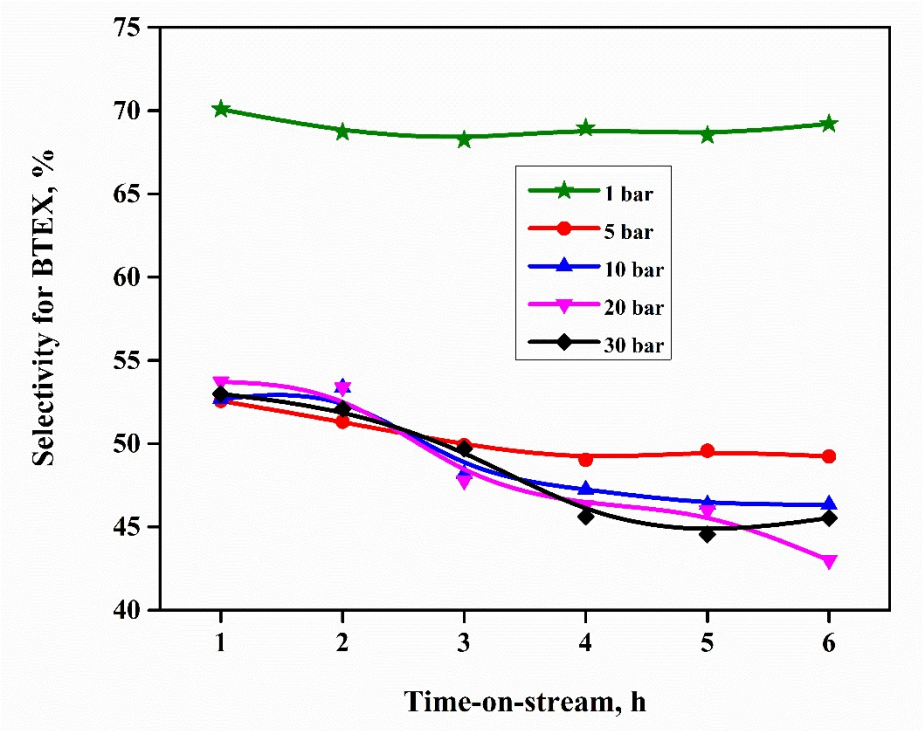


Fig. S28 Effect of pressure on BTEX selectivity over 6 h TOS, Reaction conditions: Temperature = 823 K; WHSV = 0.75 h^{-1}; 5Ga-HZSM5 catalyst.

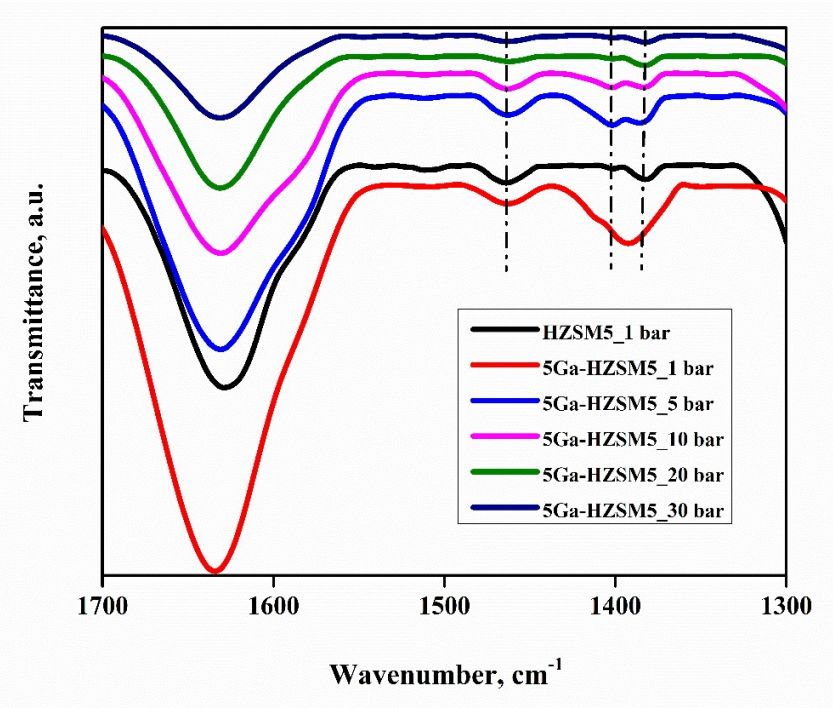


Fig. S29 FTIR spectra of spent HZSM5 and 5Ga-HZSM5 catalysts at different reaction pressure.

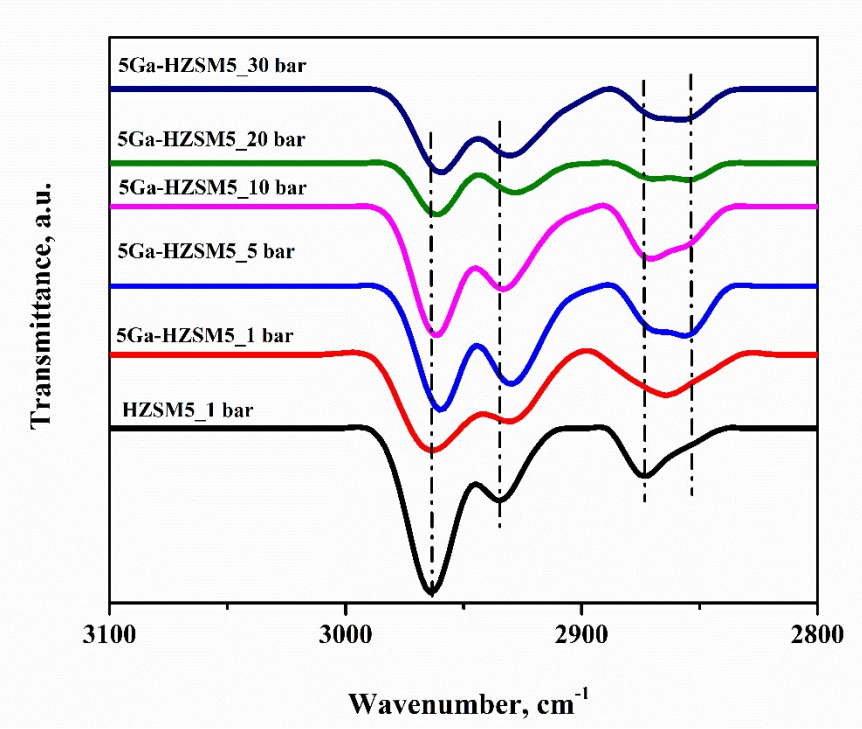


Fig. S30 FTIR spectra of spent HZSM5 and 5Ga-HZSM5 catalysts at different reaction pressure.

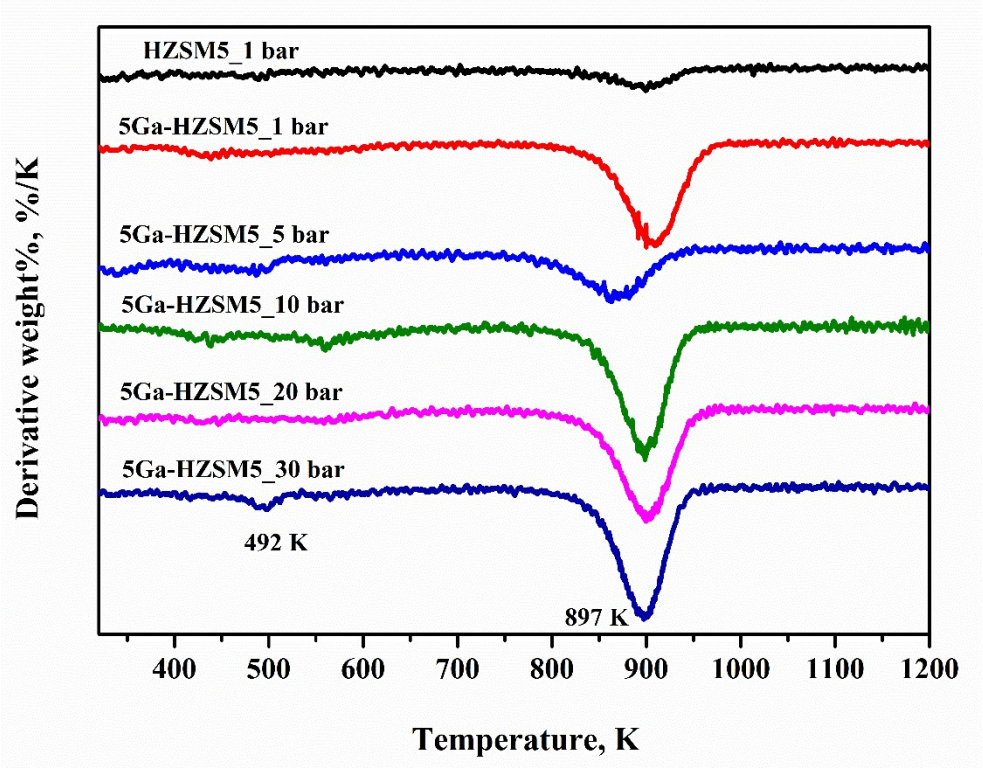


Fig. S31 DTGA analysis of spent HZSM5 and 5Ga-HZSM5 catalysts.