Electronic Supporting Information

Conversion of Bio-derived crude glycerol into renewable high-octane gasoline-stock

Vijendra Singh,[a,b] Selvamani Arumugam,[*a,b] Anup Prakash Tathod,[a,b] and Viswanadham Nagabhatla[*a,b]

a. Light Stock Processing Division, Council of Scientific & Industrial Research-Indian Institute of Petroleum, Dehradun-248005, Uttarakhand, India.

b. Academy of Scientific and Innovative Research (AcSIR) at CSIR-Indian Institute of Petroleum, Dehradun-248005, Uttarakhand, India.

Corresponding Authors E-mail: a.selvamani@iip.res.in & nvish@iip.res.in Tel: 91-135-2525856/827; Fax: 91-135-2660202

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Catalyst preparation

The extrudate-shaped ZSM-5 with Si/Al ratio of about 30-40 was purchased from Sud-Chemie India Pvt. Ltd. Herein, the various metal functionalized-ZSM-5 samples were prepared by incipient wetness impregnation method. To prepare the 1wt%Ga/ZSM-5, 1wt%Sn/ZSM-5 and 1wt%Zn/ZSM-5 samples, an aqueous solution containing the calculative amount of respective precursor salts namely $Ga(NO_3)_3{\cdot}H_2O$, $SnCl_2$, and $Zn(NO_3)_2{\cdot}H_2O$ were added to the ZSM-5 extrudate sample under vigorous stirring for effective mixing. Subsequently, the obtained mixture was dried at 120℃ for overnight and then calcined at 500℃ for 5 hours. The same method has been adopted for the preparation of bi-metallic ZSM-5 samples including 0.1wt%Sn-1wt%Zn/ZSM-5, 0.1wt%Ga-1wt%Zn/ZSM-5, 0.3wt%Ga-1wt%Zn/ZSM-5, and 0.5wt%Ga-1wt%Zn/ZSM-5 samples using the calculative amount of respective precursor salts. The prepared above samples have been designated as 1Zn/ZSM-5, 1Sn/ZSM-5, 1Ga/ZSM-5, 0.1Sn-1Zn/ZSM-5, 0.1Ga-1Zn/ZSM-5, 0.3Ga-1Zn/ZSM-5 and 0.5Ga-1Zn/ZSM-5 in the entire manuscript.

Reaction procedure

The production of gasoline from bio-glycerol and methanol (GMTG) reaction was conducted in a fixed bed vapor phase reactor setup shown in Fig. S1. Therein, prepared catalyst sample was loaded in the mid part of the reactor, and α-alumina was loaded top and bottom of the catalyst bed. Prior to the run, the catalyst was reduced at 420°C under a hydrogen gas flow of 6 liter/hour for 1 hour. The reaction mixture consisting of 1:2 (mole:mole) ratio of glycerol and methanol was fed into the reactor with WHSV of 2 h^{-1} in continuous flow of N_2 at flow rate of 6 liter/hour. The reaction was conducted at 420°C temperature at 1 bar pressure for 9 hours. The product formed in the reactor was cooled in line by cold-water circulating bath. The liquid product obtained from high-pressure separator was collected in an atmospheric tank and was analyzed using Bruker gas chromatograph (456-GC DHA) equipped with Rt-QPLOT column connected to flame ionization detector (FID) with Carboxen 1000 packed Column (60/80, 15 ft × 1/8 in. × 2.1 mm SS, Supelco). The theoretical response factor of the FID equipped in the analyzer was 0.95 ± 0.05, as mentioned in ASTM D6730-01 (2016), aqueous phase analysis done in HPLC Bio-Rad Aminex HPX-87H column (300 x 7.8 mm),df-9 µm. The gaseous product formed in the reaction was collected in a Tedlar gas bag and analyzed by SCION 456-GC instrument equipped with Hayesep Q 80/100 Mesh 1.5m x 1/16" X 1.0 mm and SCION Al_2O_3/Na_2SO_4 plot 25mx0.32 mm, df-5µm columns using ASTM-D7833 method.

The conversions of the reactant mixture and product yields were calculated using the following equations:

$$Conversion\ (C\%) = \frac{Moles\ of\ carbon\ in\ the\ converted\ reactants}{Moles\ of\ carbon\ in\ the\ feed\ mixture} x\ 100$$

$$Carbon\ yield\ of\ product\ (C\%) = \frac{moles\ of\ carbon\ in\ the\ specific\ product}{moles\ of\ carbon\ in\ the\ feed} x\ 100$$

$$Carbon\ fraction\ of\ specific\ product\ (\%) = \frac{carbon\ yield\ of\ specific\ product}{carbon\ yield\ of\ total\ hydrocarbons\ in\ liquid\ or\ gas\ products} x\ 100$$

Catalyst Characterization Methods

X-ray diffraction (XRD) patterns of the prepared catalyst sample were recorded with a PROTO bench-top X-ray diffractometer with Cu Kα radiation with 2θ = 5−80° with a scanning rate of 0.04°. FT-IR spectroscopy was conducted using Nicolet 8700 FT-IR spectrometer by the KBr method. The transmission electron microscopy (TEM) images, EDX, and elemental mapping were recorded using a JEOL JEM 2100 microscope at the accelerating voltage of 200 kV. The N_2-adsorption-desorption-isotherms of the sample were obtained from Micromeritics TriStar 3000 chemisorption instrument; all the samples were degassed at 300 ˚C for 12 hours prior to the analysis. The acidity of the prepared samples was estimated by NH_3-TPD using Micromeritics chemisorbs 2750 pulse instrument. The type of acidity present in the samples was analyzed by Pyridine-IR spectroscopy using DIGILAP, Randolph, MA. USA, MOD-FTS 300001002212, S.N. 01002210897 instrument. The thermal stability of the fresh catalyst samples and coke lay-down on the spent catalysts were measured by Thermo Gravimetric Analysis (TGA) using the DTG60 unit (Shimadzu, Japan). XPS analysis was performed with a Thermo scientific and Modale no. is NEXSA surface analysis with a micro-focused (400um, 72 W, 12000 V) monochromatic Al-Kα source (hv = 1486.6 eV), a hemispherical analyzer, and a 128 channel plate detector. ICP-AAS analysis performed with thermo scientific model iCE FIOS S/N: 5070/0921 instrument.

Table S1 Literature comparison with the present study

S. No	Reactant Mixture (Wt%)	Catalyst	T (°C)	P (bar)	WHSV (h^{-1})	TOS (h)	Total aromatics yield (C%)	Ref.
1	Glycerol (40)+Methanol(60)	HZSM-5	400	1	0.71	1.5-2	36	(1)
2	Glycerol (40)+ Methanol(60)	Sn/HZSM-5	400	1	0.71	1.5-2	43	(1)
3	Glycerol (40)+ Methanol(60)	1.23Zn/Sn/HZSM-5	400	1	0.71	1.5-2	48	(1)
4	Glycerol (40)+ Methanol(60)	HZSM-5	400	1	0.83	1-1.5	30	(2)
5	Glycerol (40)+ Methanol(60)	Zn/ZSM-5(PM)	400	1	0.83	1-1.5	47.3	(2)
6	Glycerol (40)+ Methanol(60)	Zn/ZSM-5(IM)	400	1	0.83	1-1.5	48	(2)
7	Glycerol (40)+ Methanol(60)	HZSM-5	400	1	1.07	2.5	34	(3)
8	Glycerol (40)+ Methanol(60)	Zn/HZSM-5	400	1	1.07	2.5	45	(3)
9	Glycerol (40)+ Methanol(60)	Sn/HZSM-5	400	1	1.07	2.5	42	(3)
10	Glycerol (40)+ Methanol(60)	HZSM-5	400	1	0.71	-	35	(4)
11	Glycerol (40)+ Methanol(60)	NH_4OH/HZSM-5	400	1	0.71	-	36	(4)
12	Glycerol (40)+ Methanol(60)	HZSM-5	400	1	0.71	-	36	(5)
13	Glycerol (40)+ Methanol(60)	HNO_3/HZSM-5	400	1	0.71	-	40	(5)
14	Glycerol (19.3)+ Methanol(80.7)	HZSM-5	400	0.45	0.8	-	45	(6)

15	Glycerol (40)+ Methanol(60)	HZSM-5	400	1	0.9	-	17.8	(7)
16	Glycerol (40)+ Methanol(60)	H[Sn,Al]ZSM-5	400	1	0.9	-	32.1	(7)
17	*Glycerol (58)+ Methanol(42)*	*0.1Ga-1Zn/ZSM-5*	*420*	*1*	*2*	*3-6*	*56.8*	*This Work*

(T-Temperature, P-Pressure, WHSV-Weight Hourly Space Velocity, TOS-Time-On-Stream)

Table S2 Physico-chemical properties of catalyst samples

Sample	**[a]BET surface area ($m^2.g^{-1}$)**	**[b]Zn (wt%)**	**[c]Sn (wt%)**	**[d]Ga (wt%)**	**[e]Zn (wt%)**	**[f]Sn (wt%)**	**[g]Ga (wt%)**
ZSM-5	274	--	--	--	--	--	--
1Zn/ZSM-5	266	0.98	--	--	0.96	--	--
0.1Sn-1Zn/ZSM-5	265	0.96	0.080		0.94	0.060	
0.1Ga-1Zn/ZSM-5	266	0.93	--	0.092	0.95	--	0.093

(a)-Obtained from N_2-adsorption-desorption analysis; (b-d)-obtained by EDX analysis and (e-g)-obtained by ICP-AAS analysis

Table S3 Gas product distribution

Carbon fraction (%)	**Catalyst**							
	A	**B**	**C**	**D**	**E**	**F**	**G**	**H**
$CO + CO_2$	6.6	5.7	31.3	22.9	20.4	7.6	14.6	18.3
C_1	7.3	7.7	13.5	9.6	10.4	9.3	5.8	4.5
C_2	1.0	2.0	1.8	3.2	2.4	3.4	2.0	4.9
C_2=	4.6	6.5	4.0	10.4	6.0	10.6	8.7	8.5
C_3	27.7	29.6	23.9	19.3	27.6	26.3	28.3	22.4
C_3=	1.0	0.7	10.4	9.4	14.0	18.6	16.7	14.2
iC_4	23.7	18.2	10.1	14.0	11.2	13.6	13.3	17.0
C_4	22.7	26.8	4.1	7.2	5.6	8.5	8.3	8.1
C_5	5.4	2.8	0.9	4.0	2.4	2.1	2.3	2.1
Total	100	100	100	100	100	100	100	100
H_2 gas (mol%)	10	23	17	19	34	36	35	38

Catalyst: A - ZSM-5, B - 1Zn/ZSM-5, C - 1Sn/ZSM-5, D - 1Ga/ZSM-5, E - 0.1Sn-1Zn/ZSM-5, F - 0.1Ga-1Zn/ZSM-5, G - 0.3Ga-1Zn/ZSM-5 & H - 0.5Ga-1Zn/ZSM-5

Reaction conditions: Feed: glycerol to methanol ratio of 1:2 (mole:mole), Reaction temperature: 420 °C, WHSV: 2 h^{-1}, pressure: 1 bar, and reaction time: 3-6 hrs

Table S4 Comparison of gasoline properties with BS-VI standard gasoline

Fuel parameter	**Catalyst (present study)**								**BS-VI Standard**
	A	**B**	**C**	**D**	**E**	**F**	**G**	**H**	
Density (g/ml)	0.848	0.850	0.848	0.847	0.849	0.853	0.853	0.853	0.860
IBP (˚C)	47	47	47	47	47	47	47	47	45
FBP (˚C)	235	245	199	187	236	235	237	237	210
RON	84	86	87	84	89	97	96	98	91
AKI	76	76.5	75.9	72.2	81	88	87	86	81

Catalyst: A - ZSM-5, B - 1Zn/ZSM-5, C - 1Sn/ZSM-5, D - 1Ga/ZSM-5, E - 0.1Sn-1Zn/ZSM-5, F - 0.1Ga-1Zn/ZSM-5, G - 0.3Ga-1Zn/ZSM-5 & H - 0.5Ga-1Zn/ZSM-5

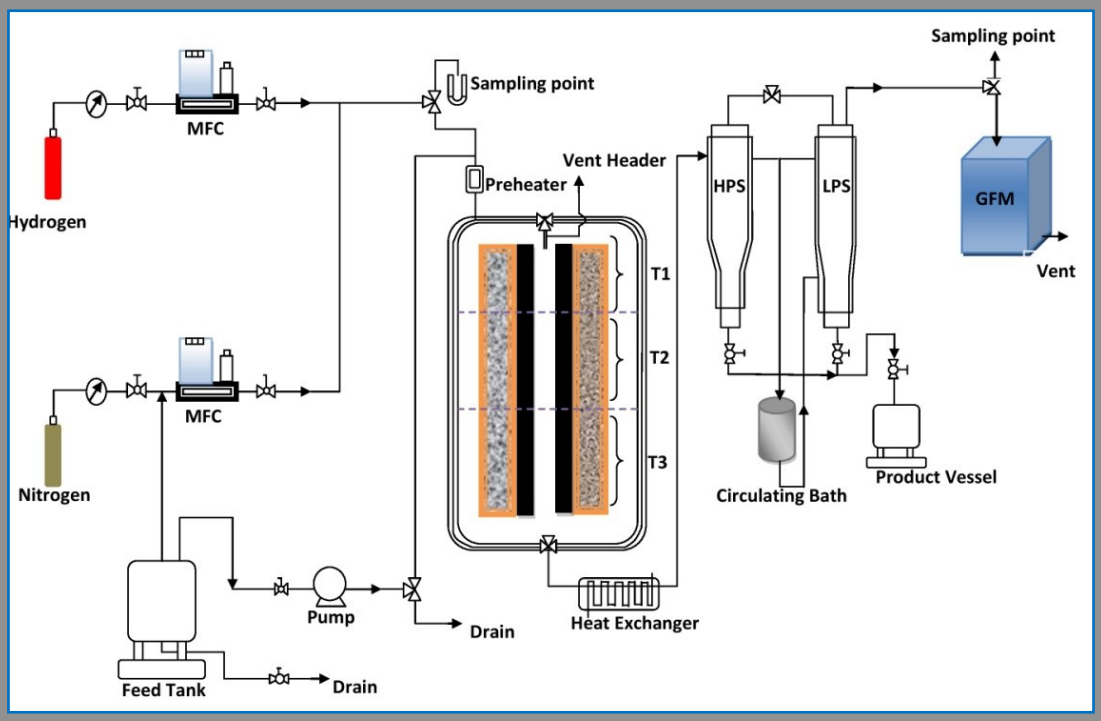


Fig. S1 Flow diagram of fixed bed down-flow reactor setup

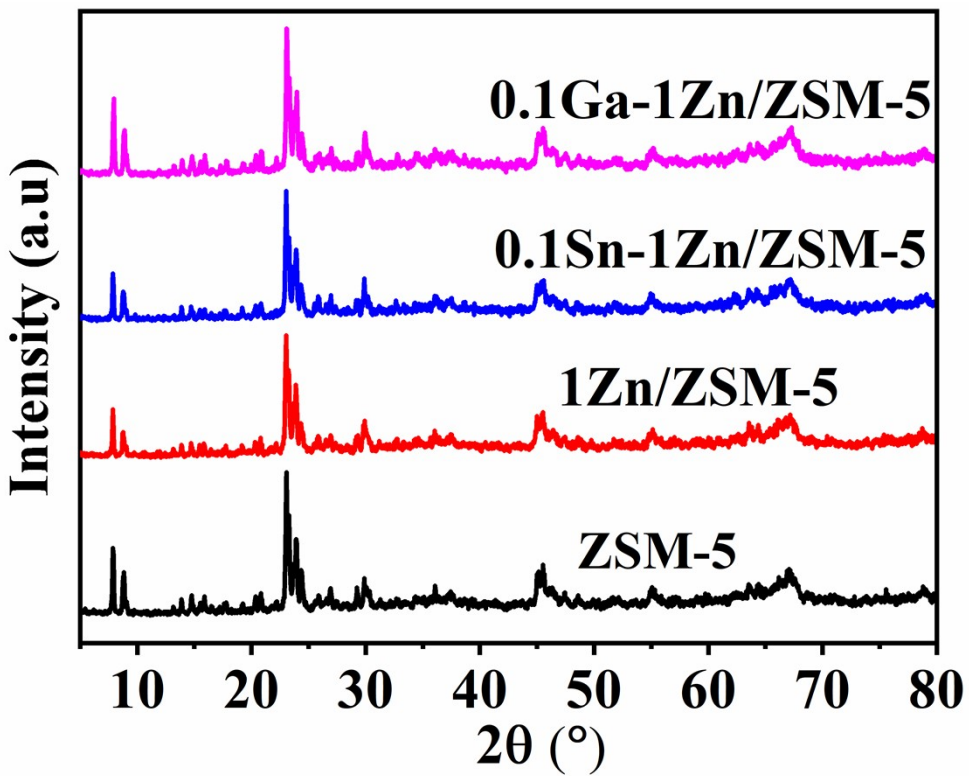


Fig. S2 XRD patterns of catalyst samples

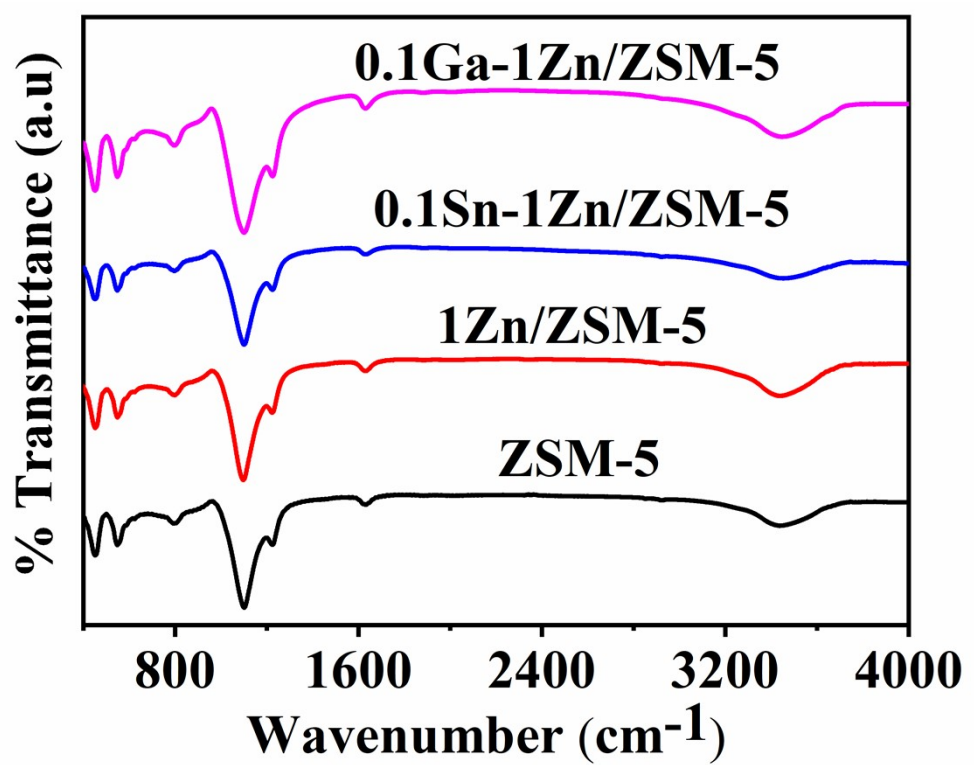


Fig. S3 FT-IR spectra of catalyst samples

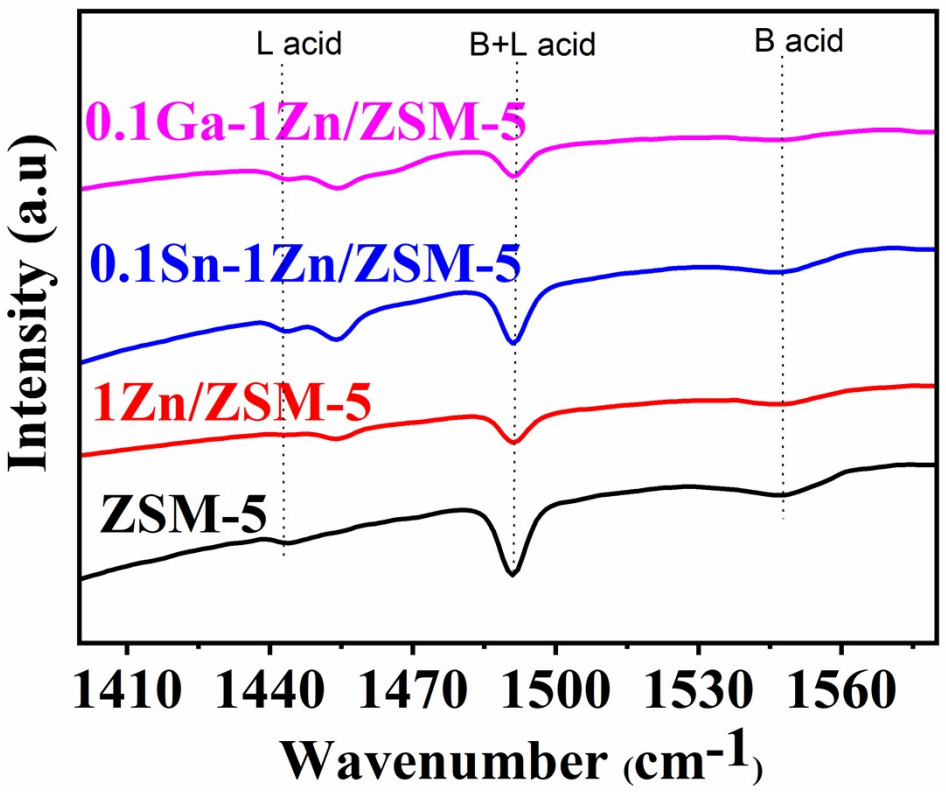


Fig. S4 Pyridine-IR spectra of catalyst samples

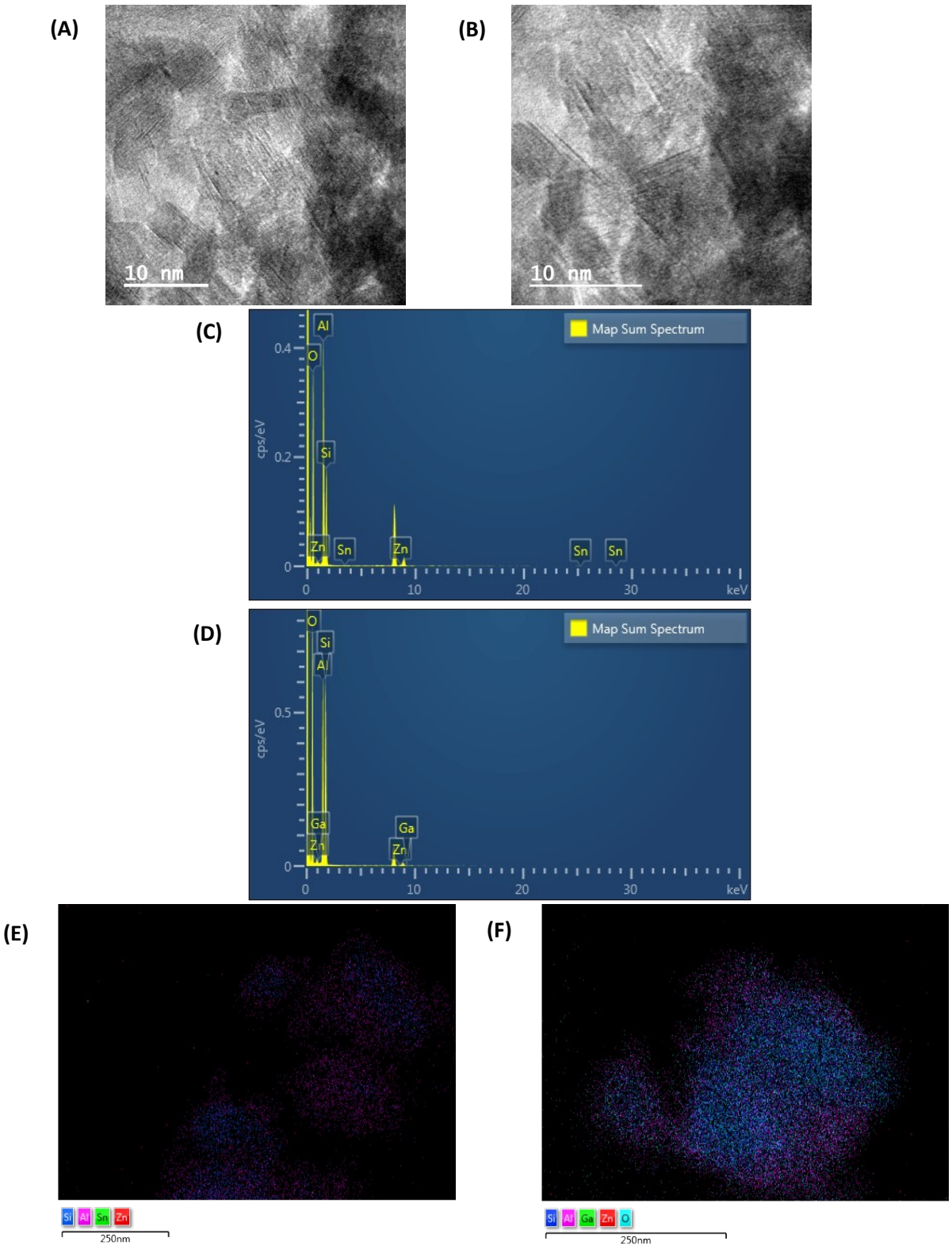


Fig. S5 TEM image of (A) 0.1Sn-1Zn/ZSM-5 & (B) 0.1Ga-1Zn/ZSM-5; EDX spectrum of (C) 0.1Sn-1Zn/ZSM-5 & (D) 0.1Ga-1Zn/ZSM-5; and Elemental mapping image of (E) 0.1Sn-1Zn/ZSM-5 & (F) 0.1Ga-1Zn/ZSM-5

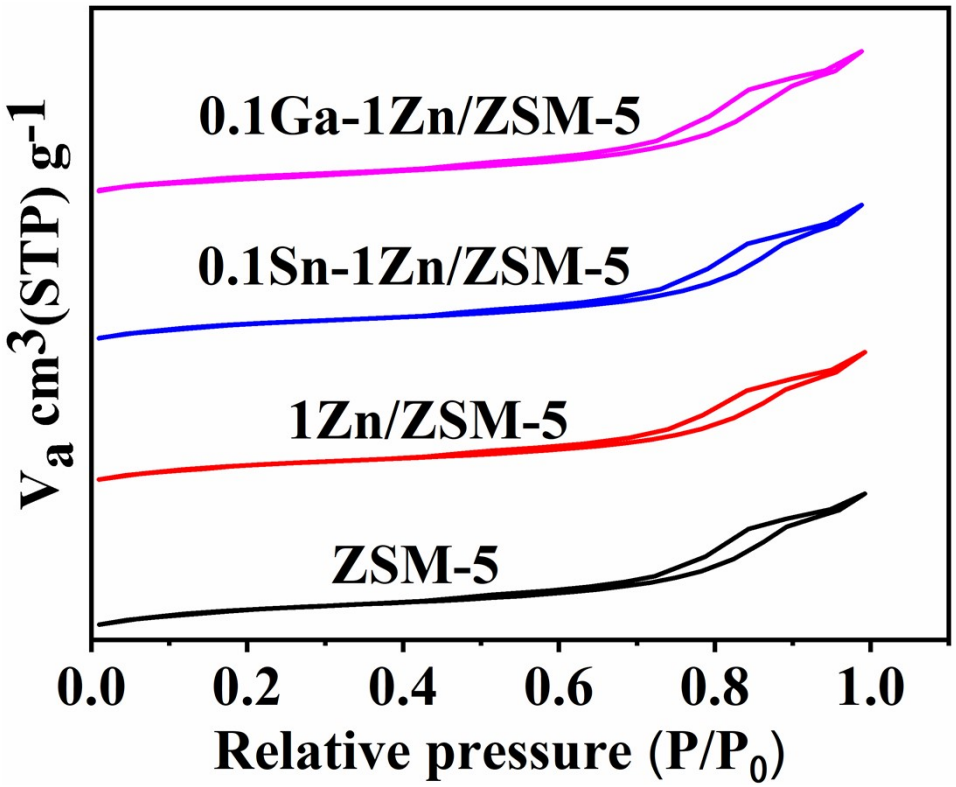


Fig. S6 N_2-adsorption-desorption-isotherms of the catalyst samples

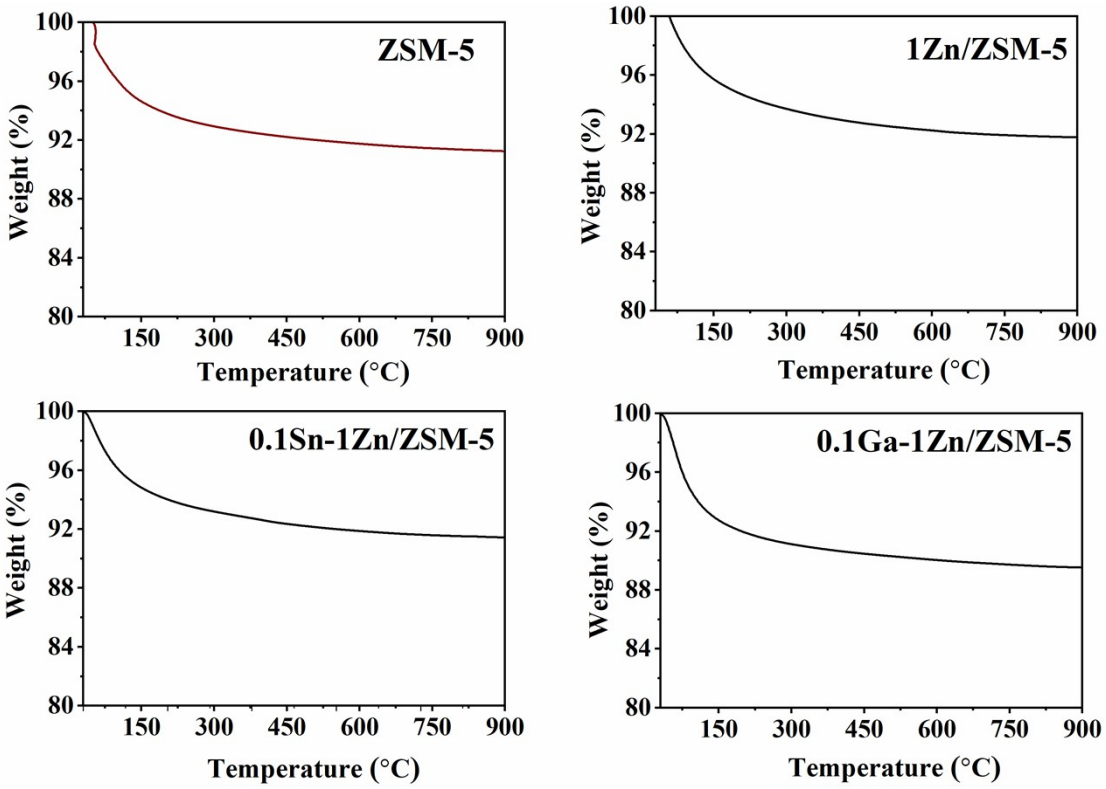


Fig. S7 TGA results of fresh catalyst samples

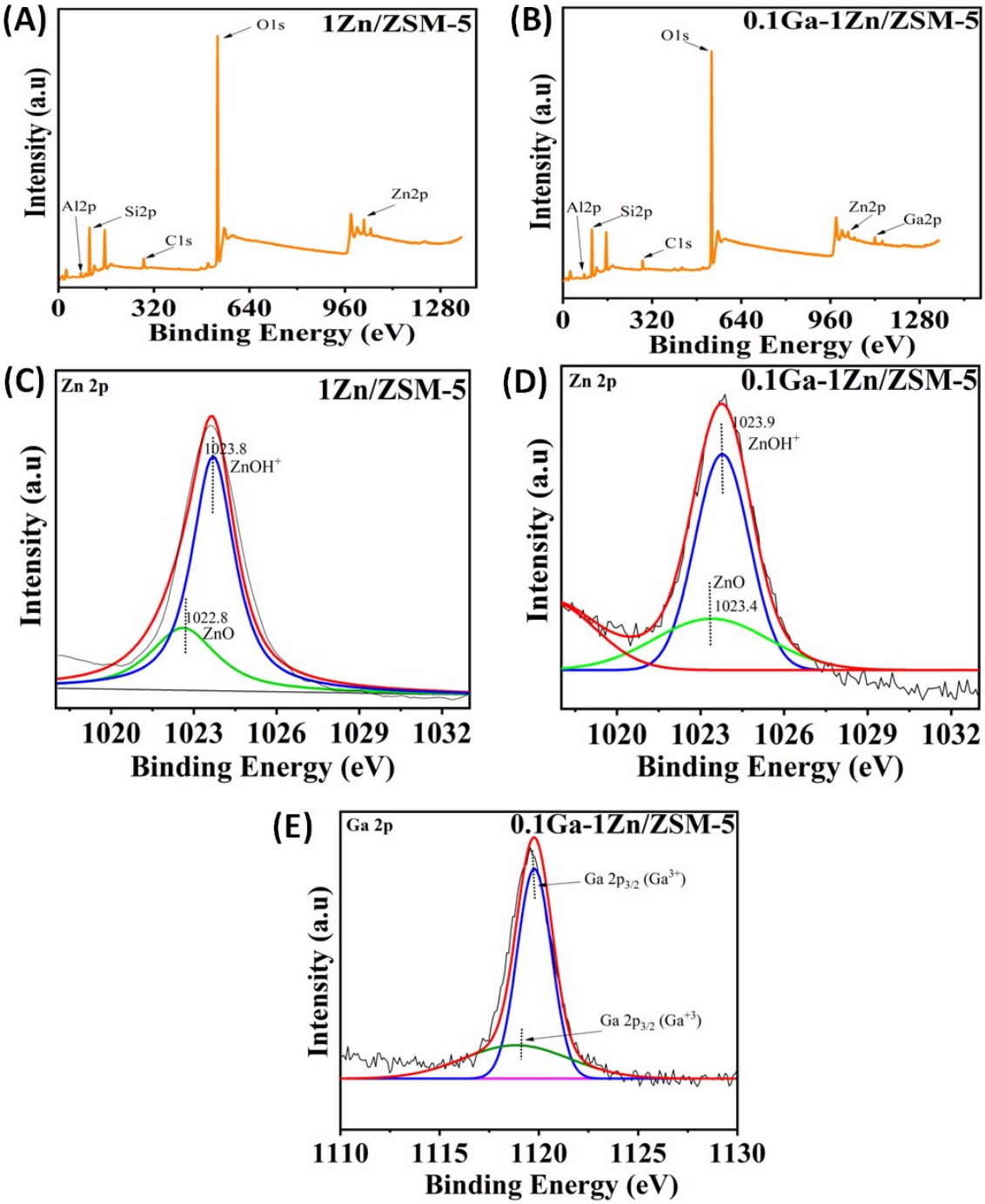
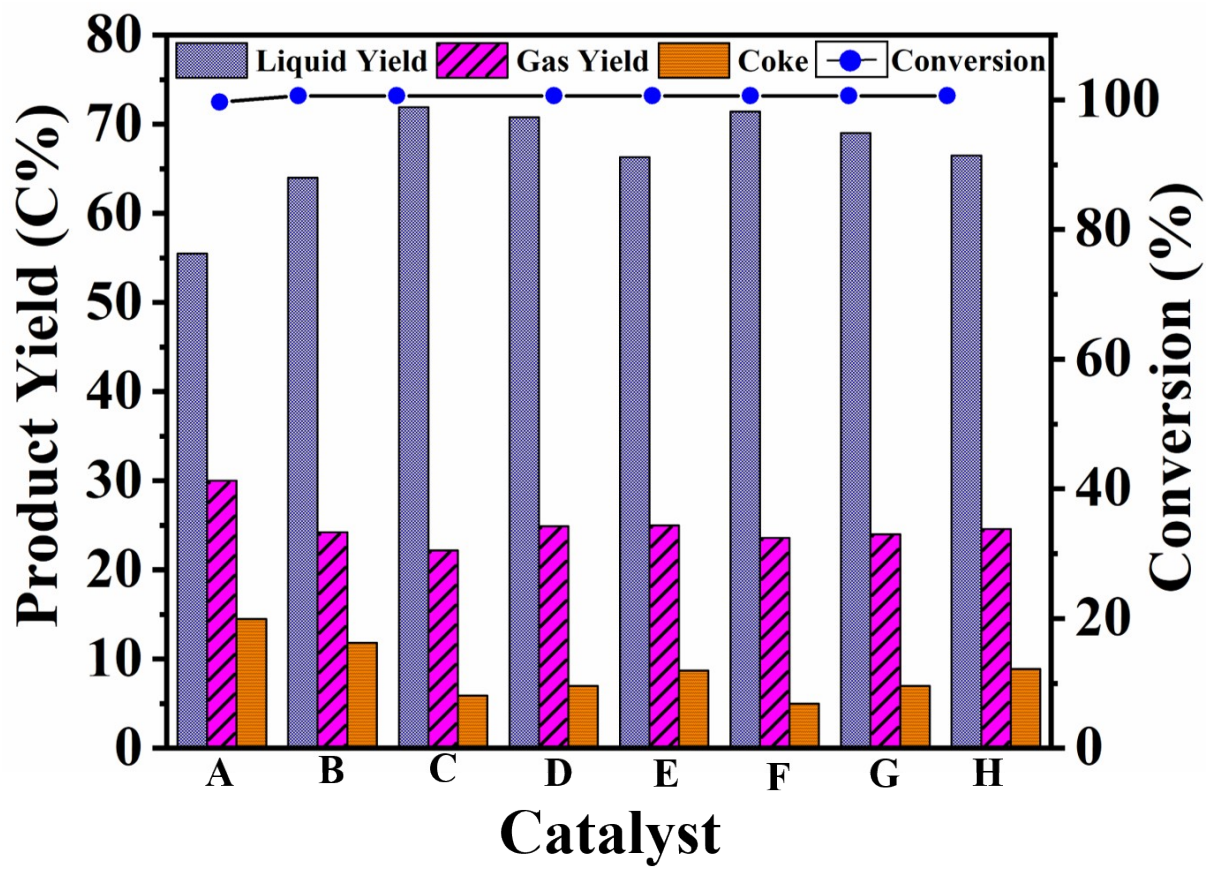


Fig. S8 XPS results (A) survey spectrum of 1Zn/ZSM-5, (B) survey spectrum of 0.1Ga-1Zn/ZSM-5, (C) Zn2p spectrum of 1Zn/ZSM-5, (D) Zn2p spectrum of 0.1Ga-1Zn/ZSM-5 and (E) Ga2p spectrum of 0.1Ga-1Zn/ZSM-5



Catalyst: A - ZSM-5, B - 1Zn/ZSM-5, C - 1Sn/ZSM-5, D - 1Ga/ZSM-5, E - 0.1Sn-1Zn/ZSM-5, F - 0.1Ga-1Zn/ZSM-5, G - 0.3Ga-1Zn/ZSM-5 & H - 0.5Ga-1Zn/ZSM-5

Reaction conditions: Feed: glycerol to methanol ratio of 1:2 (mole:mole), Reaction temperature: 420 ℃, WHSV: 2 h^{-1}, pressure: 1 bar, and reaction time: 3-6 hrs

Fig. S9 Material balance of GMTG products

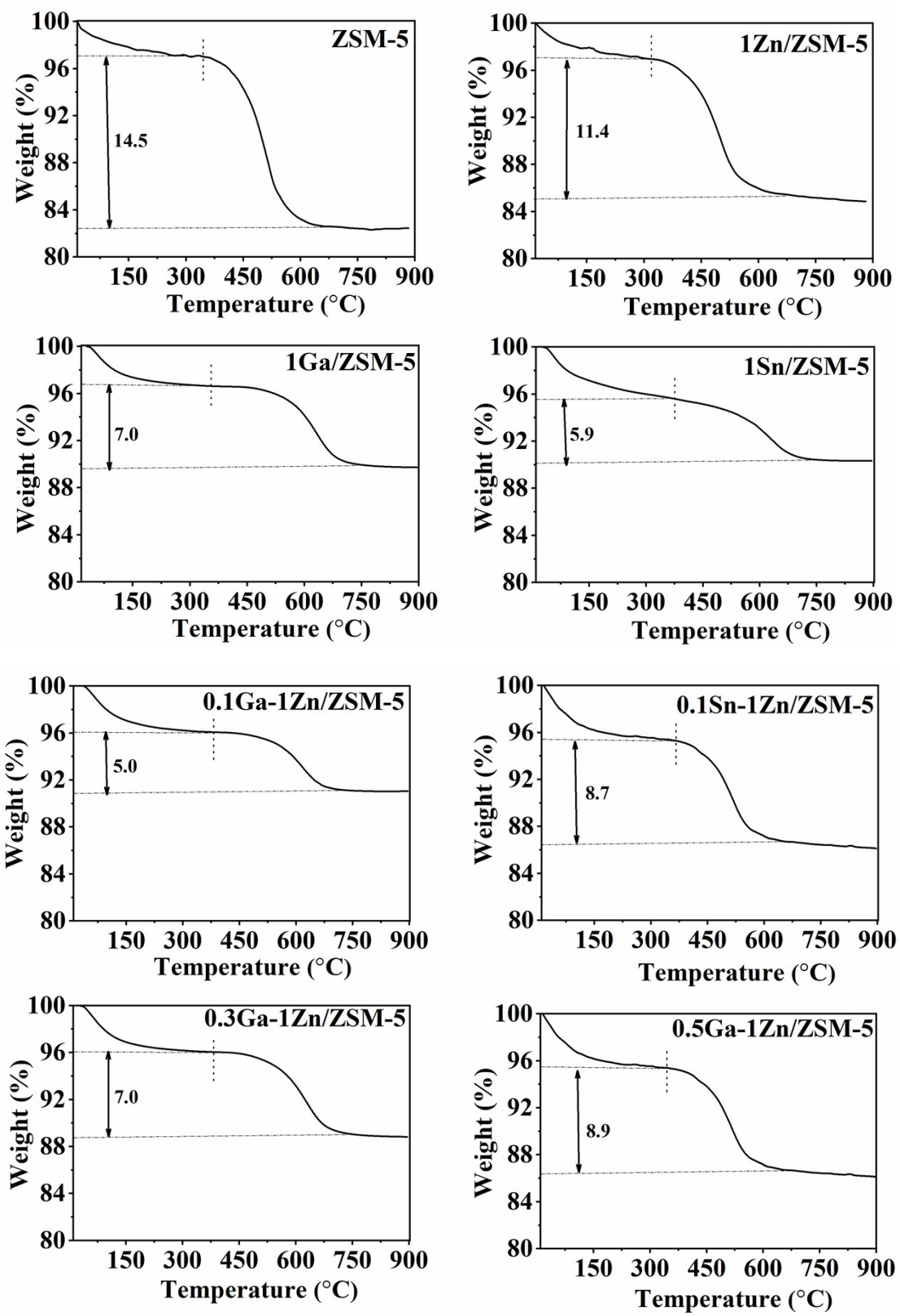


Fig. S10 TGA results of spent catalyst samples

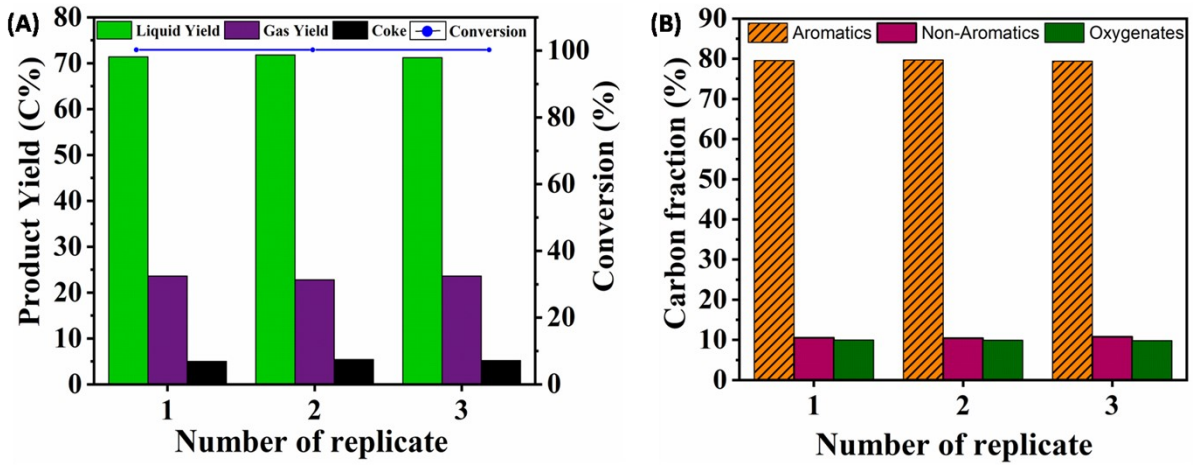


Fig. S11 Reproducibility result of 0.1Ga-1Zn/ZSM-5 (A) Product yield and (B) Aromatics selectivity

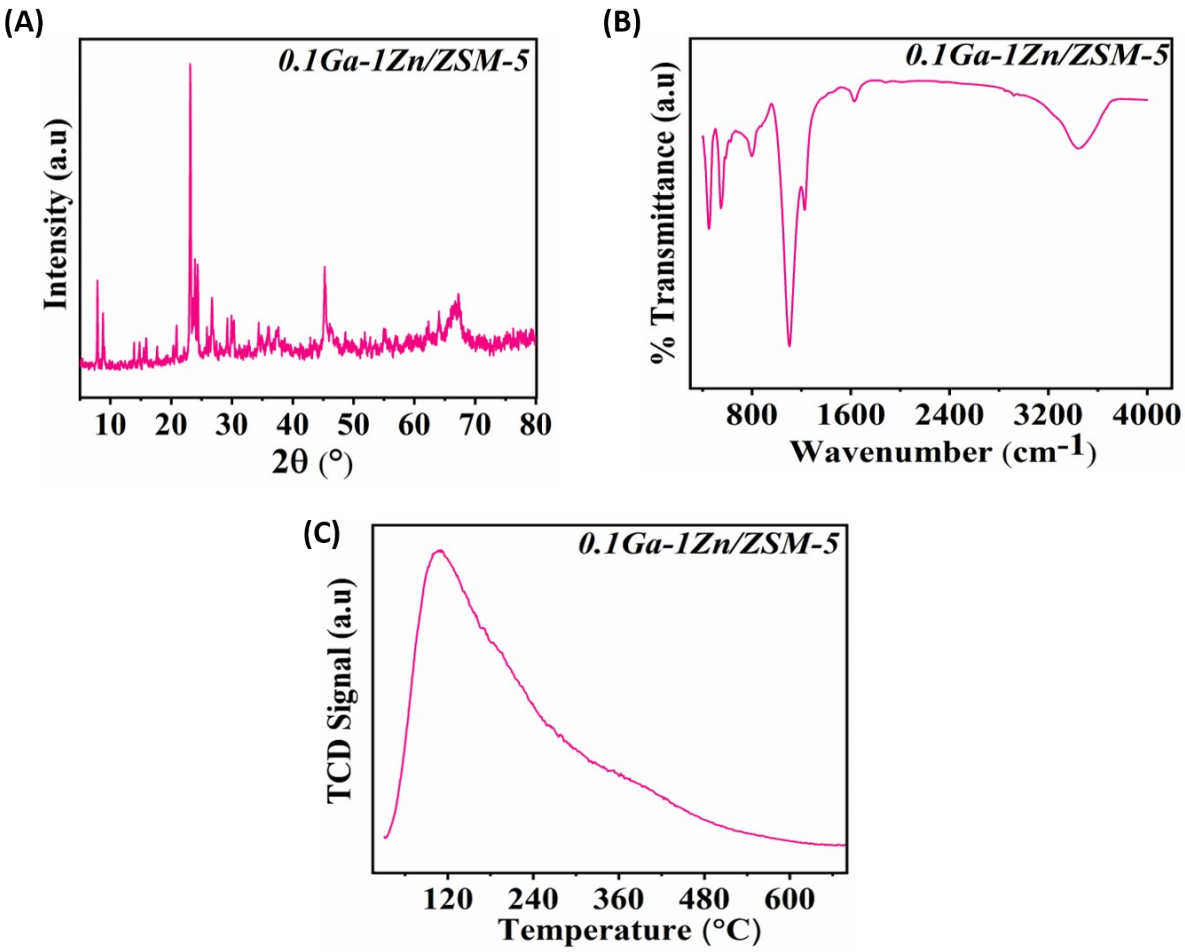


Fig. S12 Spent catalyst results (A) XRD, (B) FT-IR and (C) NH_3-TPD

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Notes and references

1. F. Wang, X. Kang, M.-x. Zhou, X.-h. Yang, L.-j. Gao and G.-m. Xiao, *Appl. Catal. A: Gen.,* 2017, **539**, 80-89.
2. D. Pan, S. Xu, Y. Miao, N. Xu, H. Wang, X. Song, L. Gao and G. Xiao, *Catal. Sci. Technol.,* 2019, **9**, 739-752.
3. F. Wang, W. Xiao, L. Gao and G. Xiao, *RSC Adv.,* 2016, **6**, 42984-42993.
4. F. Wang, M.-x. Zhou, X.-h. Yang, L.-j. Gao and G.-m. Xiao, *Mol. Catal.*, 2017, **432**, 144-154.
5. F. Wang, X. Chu, F. Zhu, F. Wu, Q. Li, B. Liu and G. Xiao, *Microporous Mesoporous Mater.*, 2019, **277**, 286-294.
6. H.-S. Jang, K. Bae, M. Shin, S. M. Kim, C.-U. Kim and Y.-W. Suh, *Fuel*, 2014, **134**, 439-447.
7. X. Yang, F. Wang, R. Wei, S. Li, Y. Wu, P. Shen, H. Wang, L. Gao and G. Xiao, *Microporous Mesoporous Mater.*, 2018, **257**, 154-161.