

Supplementary Information

Enhanced one-pot selective conversion of cellulose to ethylene glycol over NaZSM-5 supported metal catalysts

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1. NH₃- TPD

Acidity of the catalyst was examined by NH₃-temperature programmed desorption using Micromeritics Autochem-2920 instrument (USA). Around 50 mg of the sample was taken and pre-treated under helium atmosphere at 300°C with constant flow rate (20 mL.min⁻¹) for 30 min which was controlled by mass flow controller (Brooks). Then, temperature was brought down to 50 °C and NH₃ was adsorbed to sample surface using 10 % NH₃ in He (20 mL.min⁻¹) Pure He (20 mL.min⁻¹) was flushed for 30 min at 100 °C to remove any physisorbed NH₃ from the sample surface. The desorption of NH₃ was performed in He flow (20 mL.min⁻¹) by raising the temperature 100-900°C at 5 °Cmin⁻¹ and the desorbed NH₃ was monitored by thermal conductivity detector (TCD).

Entry No #	Catalyst	Acid Amounts (mmol NH ₃ g ⁻¹)		
		Weak <200°C	Medium 250°C-350°C	Strong >350°C
1	5%Al-8%Ni-25%W/NaZSM-5	0.64	0	0.12
2	3%Al-8%Ni-25%W/NaZSM-5	0	1.25	0.02
3	5%Al-6%Ni-10%W/NaZSM-5	1.13	0	0.15
4	8%Ni-15%W/NaZSM-5	0.23	0	0.11

Table S1. The acidity of the prepared catalysts as obtained from TPD-NH₃ analysis.

2. The reusability tests

The reusability studies of catalyst has been carried out at three different reaction conditions (at low conversion, at 6h and in long run (at 12h) to study the product distribution in the reaction. The catalyst obtained in after every run is been thoroughly washed with distilled water, dried at 110°C overnight and calcined at 550°C at 5°Cmin⁻¹ ramping rate for 4 h, in muffle furnace. The calcined sample was reduced at 400°C for 4 h under H₂ atmosphere before carrying out the next run

Run No.	Conversion (%)	Yield (%)					Total Glycols
		EG	1,2-PG	Glucose	Sorbitol	Others	
Run 0	45.56	52.9	7.8	26.0	7.4	5.9	60.7
Run 1	54.19	51.1	6.1	29.6	3.0	10.2	57.2
Run 2	66.87	32.1	20.3	29.4	1.8	16.4	52.4
Run 3	83.20	16.5	32.6	21.4	0.5	29.0	49.1

Table S2 a. The reusability studies of 5%Al-8%Ni-25%W/NaZSM-5 (Low Conversion)

(Reaction conditions : . Reaction conditions: cellulose: 0.20 g; catalyst: 0.20 g; water: 20 ml; pressure: 45 bar H₂ (at room temperature); temperature: 200 °C; time: 2 h; stirring speed: 1000 rpm.)

Run No.	Conversion (%)	Yield (%)					Total Glycols
		EG	1,2-PG	Glucose	Sorbitol	Others	
Run 0	100	74.2	8.4	12.8	2.9	1.7	82.6
Run 1	100	73.4	10.6	8.3	3.3	4.4	84.0
Run 2	100	70.5	10.2	12.3	5.0	2	80.7
Run 3	100	64.7	14.3	11.7	2.0	7.3	79.0

Table S2 b. The reusability studies of 5%Al-8%Ni-25%W/NaZSM-5

(Reaction conditions : . Reaction conditions: cellulose: 0.20 g; catalyst: 0.20 g; water: 20 ml; pressure: 40 bar H₂ (at room temperature); temperature: 220 °C; time: 6 h; stirring speed: 1000 rpm.)

Run No.	Conversion (%)	Yield (%)					Total Glycols
		EG	1,2-PG	Glucose	Sorbitol	Others	
Run 0	100%	89.0	0.8	6.5	0.4	3.3	89.8
Run 1	100%	83.6	2.0	5.5	1.2	7.7	85.6
Run 2	100%	76.1	2.6	11.6	1.7	8	78.7
Run 3	100%	57.8	13.8	20.7	3.1	4.6	71.6

Table S2 c. The reusability studies of 5%Al-8%Ni-25%W/NaZSM-5 (Long Run)

(Reaction conditions : cellulose: 0.20 g; catalyst: 0.20 g; water: 20 ml; pressure: 40 bar H₂ (at room temperature); temperature: 220 °C; time: 12 h; stirring speed: 1000 rpm.)

3. TG/DTA for fresh and spent catalyst

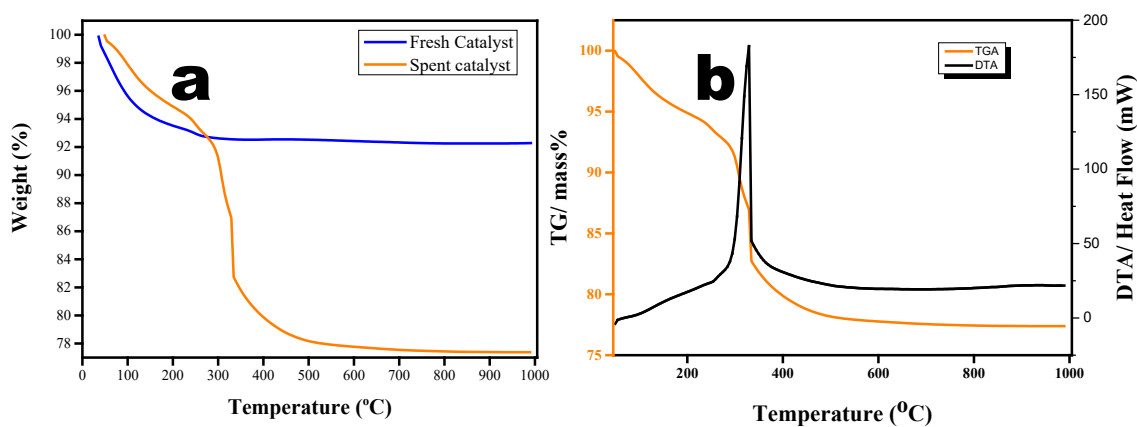


Fig. S1 : (a) TG curve for Fresh and spent catalyst (at 220°C, 70 bar H₂, 1000rpm, 6h reaction condition) (b) TG/DTA curve for spent catalyst

4. One-pot catalytic conversion of cellulose to ethylene glycol – Reaction data

Entry #	Metal Loading (%)			Support	Conversion (%)	Yield (%)					
	Al	Ni	W			EG	PG	Sor	Glu	Gly	Total Glycol [EG+PG]
1	0	8	15		100	48.8	4.23	26.97	15.37	2.53	53.03
2	0	8	20		100	51.6	3.88	21.88	19.14	2.43	55.48
3	7	8	20		100	60.9	5.11	17.35	12.04	3.03	66.01
4	5	6	10	NaZSM-5	100	61.75	4.15	17.08	13.07	-	65.9
5	5	8	20		100	67.22	6.03	10.19	12.16	-	73.25
6	5	8	25		100	70.85	9.2	2.54	12.75	0.87	80.05
7	5	8	30		100	70.45	10.07	2.33	12.97	1.05	80.52
8	5	4	25		100	19.09	20.28	-	24.63	5.51	39.37
9	5	8	25	HZSM-5	100	65.47	15.48	11.06	1.84	0.45	80.95
10	5	8	25	HZSM-5(1:1)	100	53.21	5.06	4.62	11.82	1.11	58.27

Tables 3: Hydrolytic hydrogenation reactions of cellulose to ethylene glycol carried out in 50 ml stainless steel Parr Batch reactor.

Reaction Conditions : 0.20g cellulose, 0.15gm catalyst and 20 ml water at 40 bar H₂ pressure at 220°C for 6 hours at 1000rpm.
 EG= Ethylene glycol, PG= 1,2-Propanediol, Sor= Sorbitol , Glu = Glucose, Gly= Glycerol
 Note: HZSM-5 (1:1) corresponds that equal amount of cellulose and metal loaded catalyst on HZSM-5 is been used.

5. HPLC chromatogram

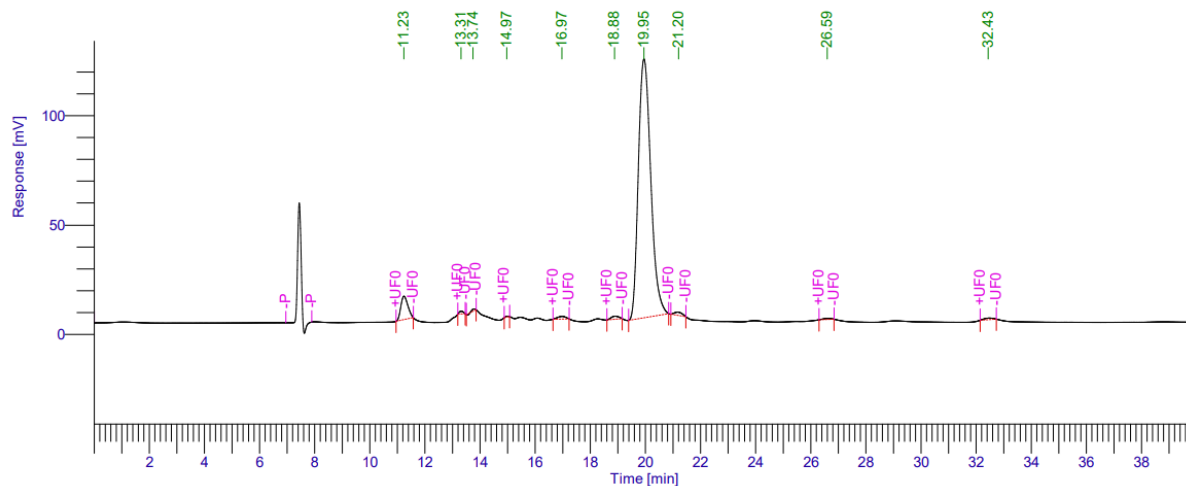


Fig. S2a : The HPLC chromatogram of 5%Al-8%Ni-25%W/NaZSM-5 catalyst on cellulose conversion for 12h,70 bar H₂ at 220°C, 1000rpm

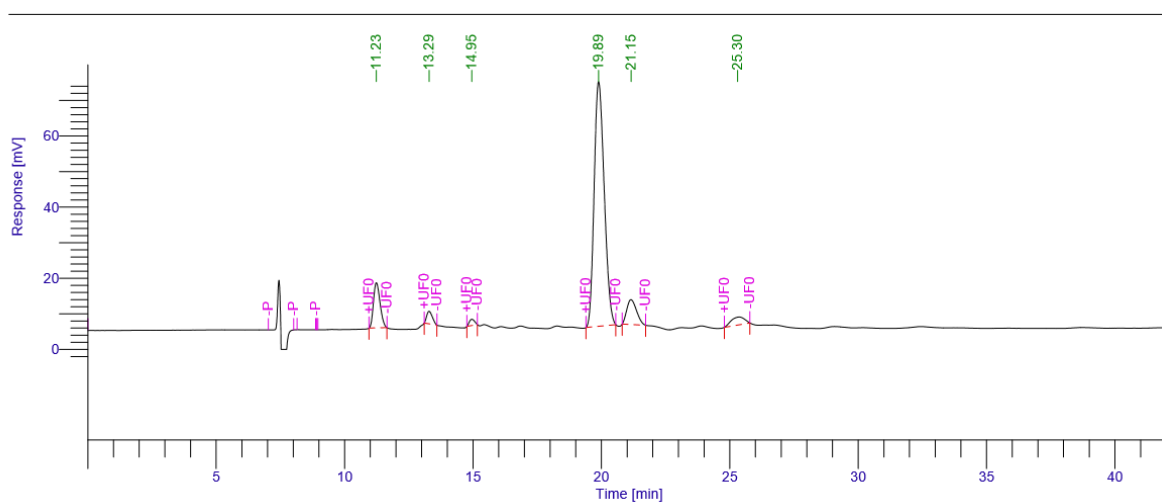


Fig. S2b : The HPLC chromatogram of 5%Al-8%Ni-25%W/NaZSM-5 catalyst on cellulose conversion for 6h,70 bar H₂ at 220°C, 1000rpm

The incorporated is the HPLC chromatogram of the one-pot catalytic conversion of cellulose to ethylene glycol over 5%Al-8%Ni-25%W/NaZSM-5 catalyst for the reaction conditions, cellulose: 0.20 g; catalyst: 0.20 g; water: 20 ml; pressure: 40 bar H₂ (at room temperature); temperature: 220 °C; time: 12 h and 6 h; stirring speed: 1000 rpm.

The peak at the retention times 19.95 correspond to the EG, 21.2 corresponds to 1,2-PDO, 11.23 corresponds to glucose, 26.59 to ethanol, 13.31 and 13.74 represents sorbitol and mannitol respectively, 14.97 is xylitol, 16.97 represents glycerol 32.43 is 2-propanol. The peak before retention time 8 is the solvent peak.

Calibration of HPLC is done by plotting the calibration curve Fig S2c. A set of 5 standard solutions of ethylene glycol has been made in 20 mL millipore water and the was injected to the HPLC separately. The analysis condition remains the same as for product analysis (Oven temperature : 60°C, Flow rate : 0.5 mL min⁻¹). The areas under the peak after each individual injections are noted. The graph is plotted against Weight of standard VS Area obtained. The slope will give the R_f factor. Thus the numbers of moles are obtained from the HPLC. And the values are substituted in the equation given in the manuscript to find out the yield. Since cellulose is the polymer of glucose, the M_c is taken as 162.14, the relative mass of one glucose unit and k_c is taken as 6. The k_i accounts for the carbon number of the product and for EG it is 2.

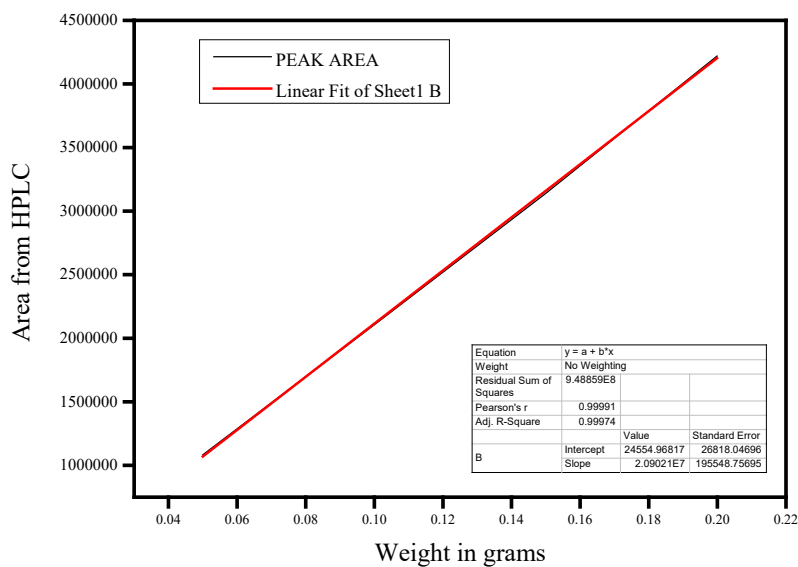


Fig. S2c :The calibration curve of the product, Ethylene glycol

6. The list of references which calculated EG yield in terms of carbon mol%

Sl No	Catalyst	Reaction Condition	EG Yield%	Reference	DOI
1	Ni-W@C	240°C, 5MPa, 1h	99% cellulose conversion and 60.1% EG	<i>Cellulose</i> 27 , 7591–7605 (2020)	https://doi.org/10.1007/s10570-020-03340-1
2	1wt% Ru /h-WO ₃	240°C, 4MPa, 2h	77.5%	Bioresource Technology 264 : 58-65 (2018)	https://doi.org/10.1016/j.biortech.2018.05.026
3	Ru/W/AC	Mix milling (4 minutes) 220°C, 6.5MPa, 3h	90% conversion with EG yield % of 34.2 %	<i>Green Chem.</i> , 2015, 17 , 3075-3083	https://doi.org/10.1039/C5GC00421G
4	1% Ru/WO ₃ nanosheet	4 MPa H ₂ , 240 °C, 2 h	76.3%	<i>Green Chem.</i> , 2017, 19 , 682-691	https://doi.org/10.1039/C6GC01327A
5	Ni–W/M	240 °C, 4 MPa H ₂ , 120 min	68.7%	<i>ACS Sustainable Chemistry & Engineering</i> 2020 <i>8</i> (26), 9650-9659	https://doi.org/10.1021/acssuschemeng.0c00836

Table S4. List of literatures reported the ethylene glycol yields in terms of C-mol %

7. The comparison of reusability of different Ni-W supported metal catalysts on EG yield on cellulose conversion.

Sl No	Catalyst	Conversion (%)	Y _{EG} ^a (%)	Reusability cycle ^b	Y _{EG} ^c (%)	Reaction Conditions	References/ DOI
1	Ni-W ₂ C/AC	100	61.0	3	51.0	245 °C and 6 MPa for 0.5h	14 10.1016/j.cattod.2009.03.012
2	Ni/W/SiO ₂ -Al ₂ O ₃	92	32.1	2	22.4	245 °C and 6 MPa for 2h	53 10.1016/j.biortech.2012.03.059
3	Ni-W/MSM ^d	100	72.9	3	45.6	245 °C and 6 MPa for 2h	54 10.1039/c8ra00584b
4	Ni/W/AC	83	47.6	2	42.2	215 °C and 6.5 MPa for 3h	42 10.1039/c4gc00664j
5	NiWB(1:1)/CNTs	100	57.7	3	48.2	250 °C and 6 MPa for 2h	55 10.1016/j.catcom.2016.01.014
6	Ni _{0.3} -W _{0.3} /CNF	95	33.6	3	21.3	245 °C and 6 MPa for 2h	56 10.1039/c6gc00703a
7	Ni-W/SiO ₂ -EEG	100	63.3	3	55.1	240 °C and 5 MPa for 2h	57 10.1016/j.fuel.2017.11.086
8	Ni-W/SiO ₂ @C-12	100	60.7	3	46.6	240 °C and 5 MPa for 1h	58 10.1007/s10562-018-2582-2
9	Ni-W/SiO ₂	100	63.1	3	57.4	240 °C and 5 MPa for 2h	59 10.1016/j.fuel.2018.04.115
10	Ni-W/MO	100	47.6	4	44.0	245 °C and 4 MPa for 2h	45 10.1021/acssuschemeng.0c00836
11	Ni-W/M	100	68.7	7	66.9	245 °C and 4 MPa for 2h	
12	Ni-W/T	100	34.5	2	26.1	245 °C and 4 MPa for 2h	
13	Ni-W-Cu/MgAl ₂ O ₄ (1:3)	100	52.8	3	42.3	245 °C and 3 MPa for 2h	37 10.1021/acsomega.1c00979
14	Al-W-Ni/TUD-1	100	76.0	2	56.1	230 °C and 4 MPa for 1.5h	21 10.1039/C7GC02122D
15	Al-W-Ni/NaZSM-5 ^d	100	74.2	4	64.7	220 °C and 4 MPa for 6h	Present work
16	Al-W-Ni/NaZSM-5 ^d	100	89.0	3	76.1	220 °C and 4 MPa for 12h	Present work

Table S5. Comparison of the reusability of different Ni-W catalysts in the conversion of cellulose to EG

^a Yield % of Ethylene glycol (Y_{EG}) after first run

^b Included only the number of cycles where the loss of EG yield of less than 30% (compared with the first run) in the recycling tests.

^c Yield % of Ethylene glycol (Y_{EG}) after mentioned number of cycles

^d Catalyst was re-calcined and re-reduced before successive runs.