Supporting Information

Mesoporous Ta_2O_5/Nb_2O_5 nanocomposite with Lewis/Brønsted acid sites to enhance stepwise glucose conversion to 5-hydroxymethylfurfural

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Total pages: 31

Total Tables: 23

Total Figures: 25

Experimental

Mathematical expressions

$$Glucose/Fructose\ conversion\ (\%) = \frac{Sugar\ reacted\ (mol)}{Initial\ sugar\ (mol)} \times 100$$

---------- (S1)

$$Product\ yield\ (\%) = \frac{Product\ formed\ (mol)}{Initial\ sugar\ (mol)} \times 100$$

---------- (S2)

$$Product\ selectivity\ (\%) = \frac{Product\ yield\ (\%)}{Sugar\ conversion\ (\%)} \times 100$$

---------- (S3)

First-order kinetic rate equation

$$ln\left\{\frac{[Sugar]_t}{[Sugar]_0}\right\} = -\ k \times time\ (sec)$$

---------- (S4)

Where, sugar can be glucose or fructose. $[Sugar]_t$ and $[Sugar]_0$ represent the final and initial reactant (sugar) concentration at time *t*. *k* is the observed rate constant of reaction (disappearance of sugar).

The temperature dependency of the rate constant, *k* was determined by using the Arrhenius equation (Eqn. S5):

$$k = A_0 \times e^{\left(-\frac{E_a}{RT}\right)}$$

---------- (S5)

where, A_0 is the frequency factor (or Arrhenius constant), E_a is the activation energy (J/mol), and *R* is the universal gas constant (8.31 J/mol. K).

The reaction's free energy change ($\Delta G°$) was calculated as:

$$\Delta G^{o} = -RT\ln\left(\frac{kh}{Tk_{B}}\right)$$

---------- (S6)

Where, $\Delta G°$ is the reaction activation free energy; k is the rate constant (s^{-1}); T is the temperature (K); k_B is the Boltzmann constant (1.381×10^{-23} J/K), h is the Planck's constant (6.626×10^{-34} J.s) and R is the universal gas constant (9.314 J/mol. K).

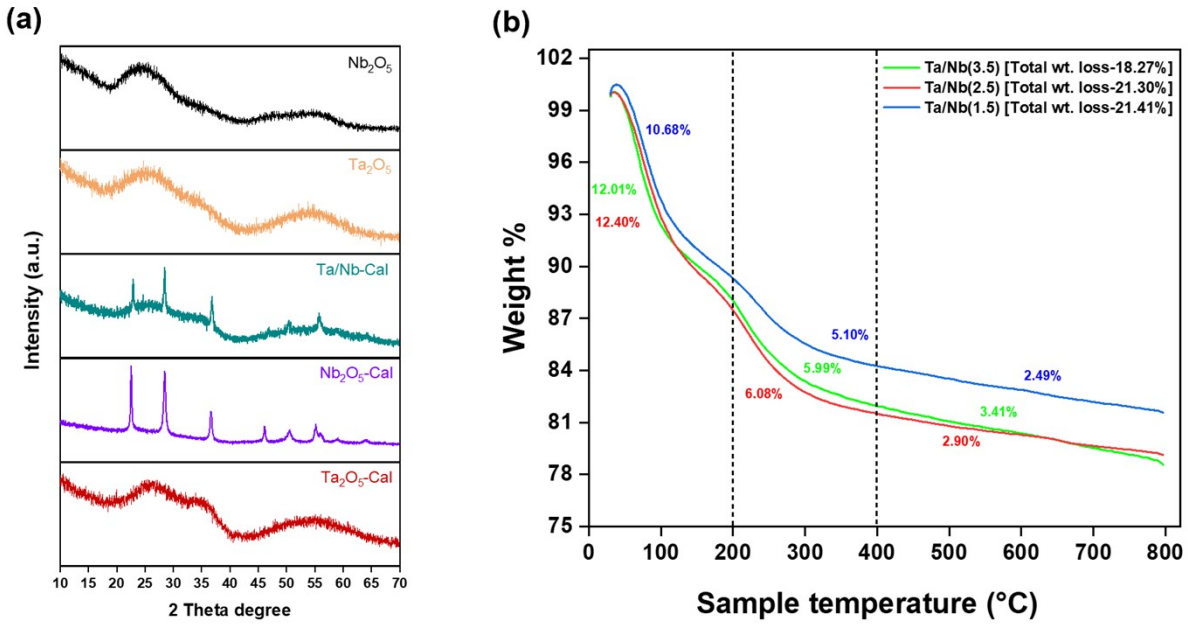

Figure S1. (a) XRD pattern of pure Ta_2O_5, Nb_2O_5 and calcined catalysts and (b) TGA curve of as-synthesized composite catalysts.

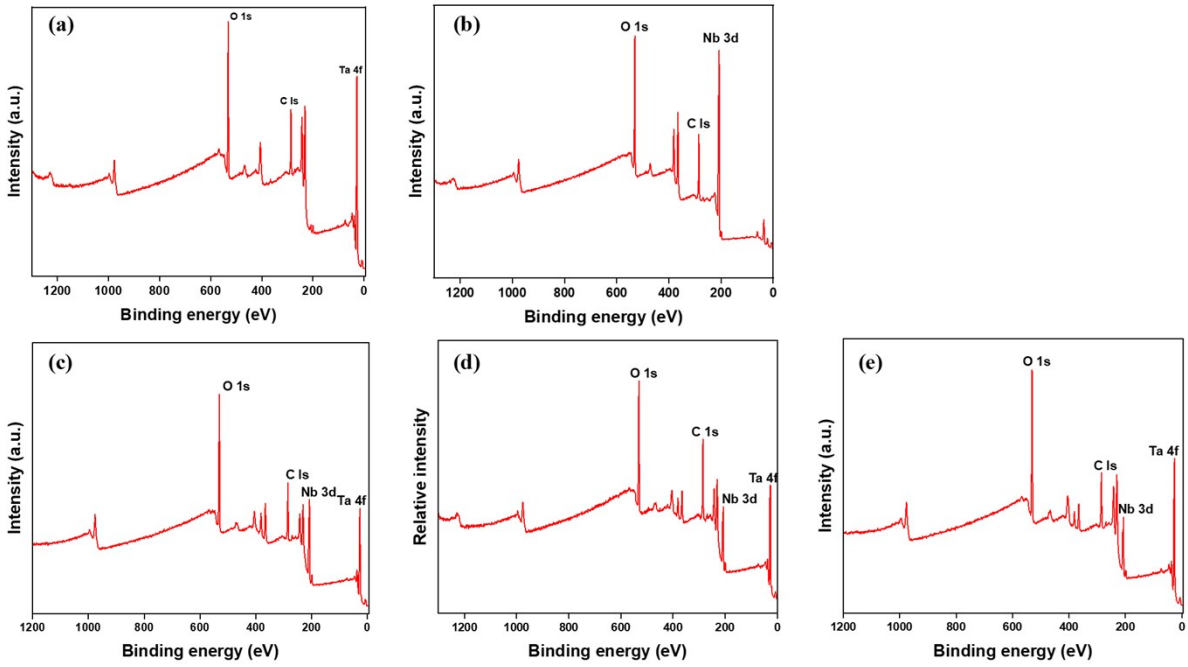

Figure S2. XPS survey spectrum of Ta_2O_5 (a), Nb_2O_5 (b), Ta/Nb-1.5 (c), Ta/Nb-2.5 (d), and Ta/Nb-3.5 (e).

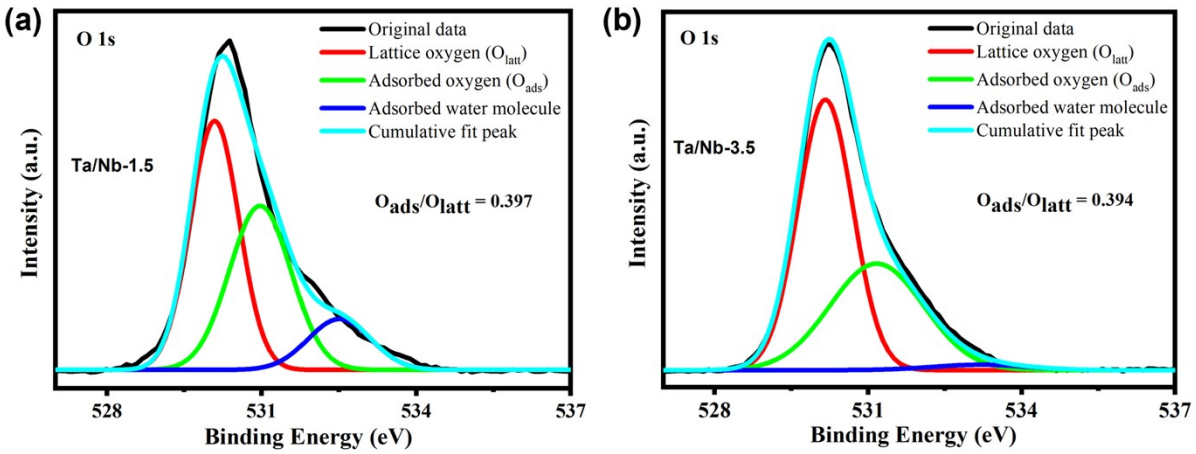

Figure S3. Deconvolution result of O 1s peak of (a) Ta/Nb-1.5 and (b) Ta/Nb-3.5 catalysts.

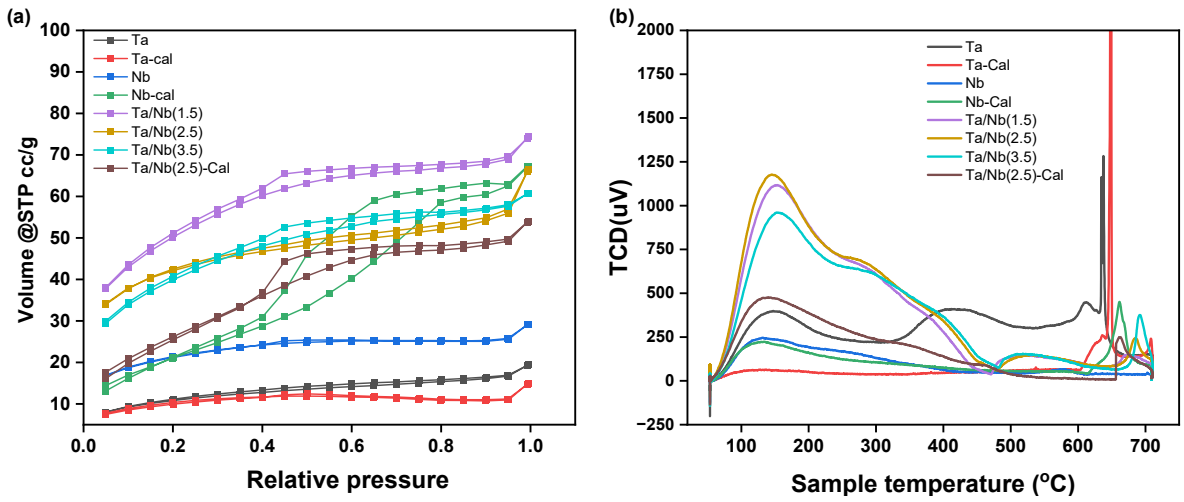

Figure S4. NH_3 TPD analysis report of as-synthesized catalysts: (a) physisorption isotherm and (b) acidic sites measurement with respect to temperature.

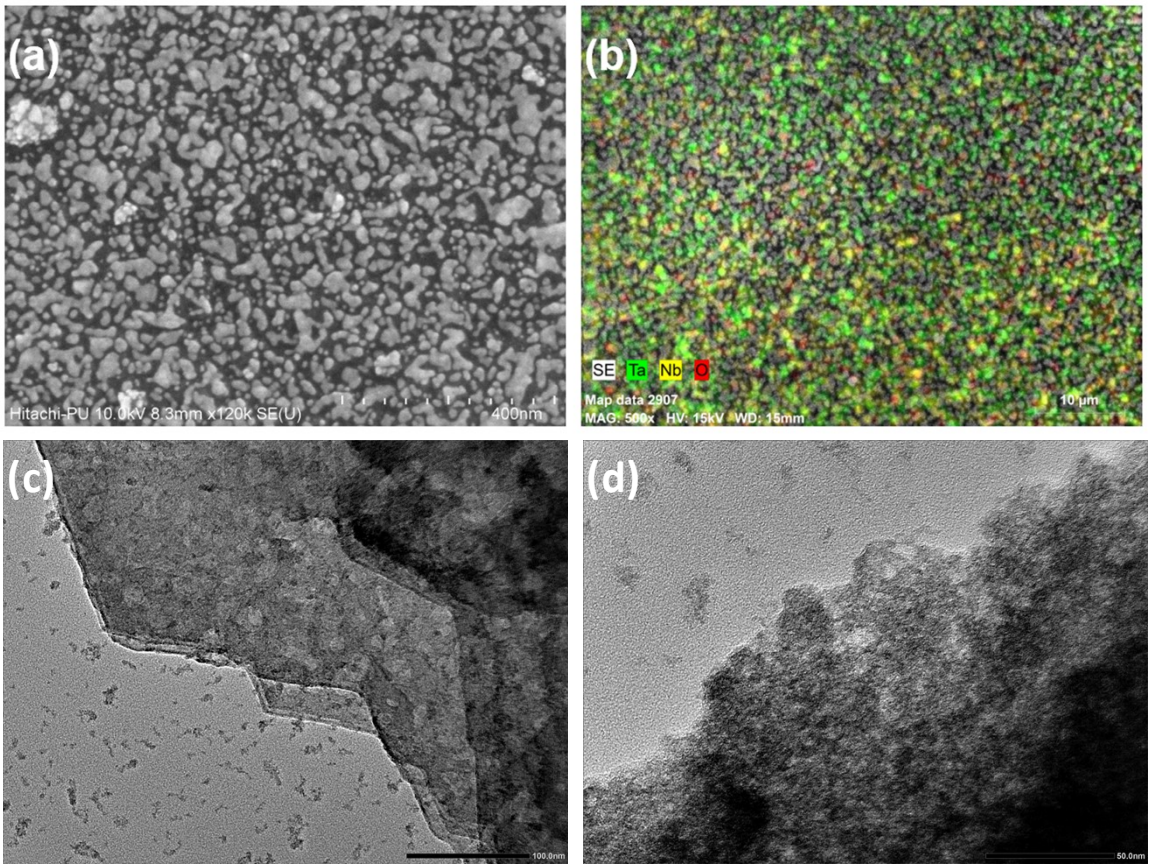

Figure S5. FE-SEM image (a), EDX mapping (b), and TEM images (c-d) of Ta/Nb-2.5.

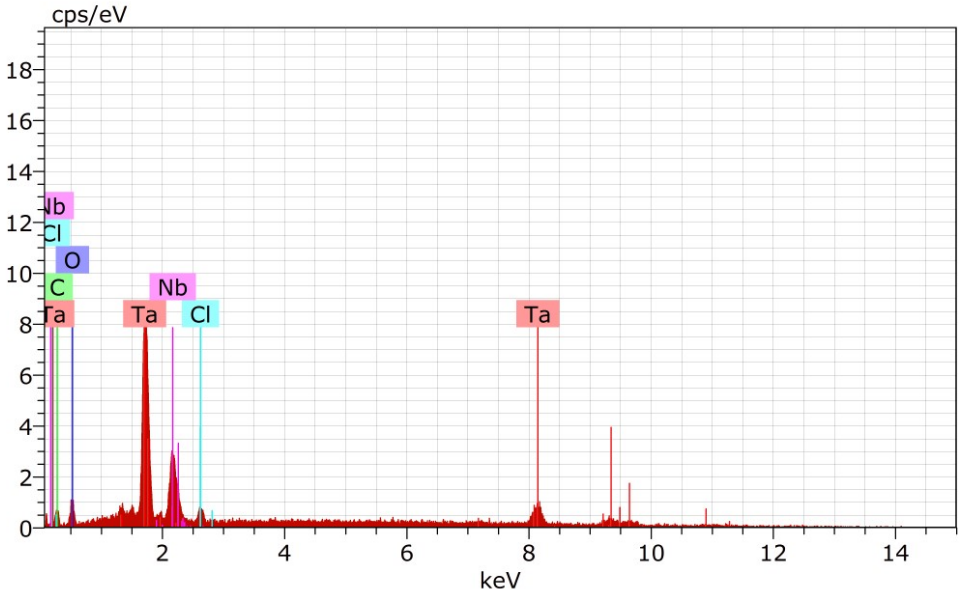

Figure S6. EDX report of as synthesized Ta/Nb-2.5.

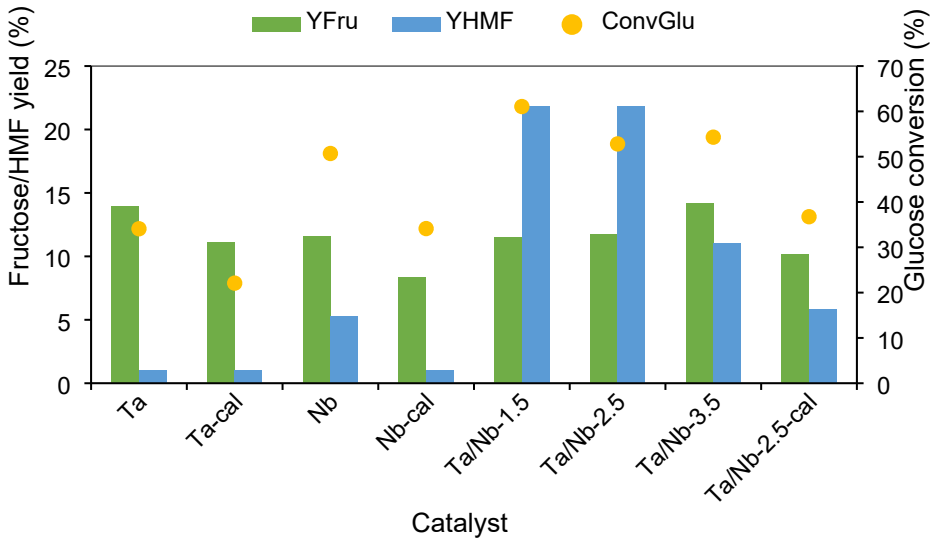

Figure S7. Catalyst's effectiveness on glucose decomposition to HMF in a water medium. Reaction conditions: 170 °C and 25% wt. catalyst load for 3 h. YFru-yield fructose, YHMF-yield HMF and ConvGlu-glucose conversion.

Table S1. Comparative result of glucose catalysis in water at 170 °C and 25% catalyst load on glucose after 180 min.

Catalysts	$Selectivity_{Fru}$	$Selectivity_{HMF}$	$Yield_{LA}$ (%)	$Yield_{FA}$ (%)	TON_{HMF} (sec^{-1})	TOF_{HMF} (10^{-6})
Ta	40.91	3.07	0.84	n.d.	0.0125	1.160
Ta-cal	50.19	0.13	n.d.	n.d.	0.0142	1.315
Nb	22.87	10.46	7.35	n.d.	0.0199	1.845
Nb-cal	24.43	0.30	1.66	n.d.	0.0143	1.326
Ta/Nb-1.5	18.90	35.75	11.06	n.d.	0.0137	1.273
Ta/Nb-2.5	22.18	41.40	10.78	n.d.	0.0132	1.228
Ta/Nb-3.5	26.05	20.35	10.72	n.d.	0.0104	0.996

N.d.-not detected. TON-turn over number is calculated as moles of reactant consumed per mole of catalyst. TOF-turn over frequency is calculated as moles of reactant consumed per mole of catalyst per unit time.

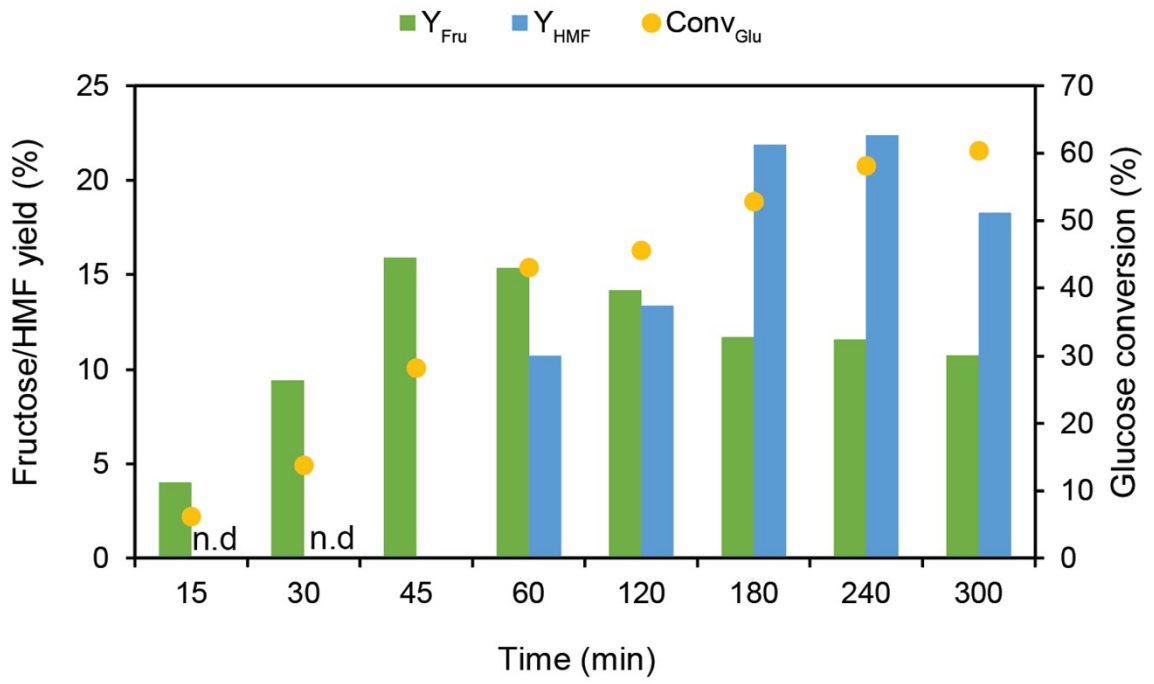

Figure S8. Time optimization of glucose decomposition to HMF in a water medium using Ta/Nb-2.5. Reaction conditions: 170 °C and 25% wt. catalyst load for 5 h. Y-yield and Conv-conversion. N.D.-not detected.

Table S2. Effect of time on dehydration of glucose to 5-HMF at 170 °C in a water medium using 25% of Ta/Nb-2.5 up to 300 min.

Time (min)	$Selectivity_{fru}$	$Selectivity_{HMF}$	$Yield_{LA}$ (%)	$Yield_{FA}$ (%)	TON_{HMF} (sec^{-1})	TOF_{HMF} (10^{-6})
15	65.00	n.d.	n.d.	n.d.	0	0
30	68.57	n.d.	n.d.	n.d.	0	0
45	56.25	0.17	n.d.	n.d.	0.0048	1.773
60	35.67	24.93	n.d.	n.d.	0.0095	2.650
120	31.06	29.25	6.09	n.d.	0.0104	1.446
180	22.18	41.40	9.45	n.d.	0.0133	1.228
240	19.96	38.53	9.80	n.d.	0.0134	0.9330
300	17.80	30.27	10.12	n.d.	0.0121	0.6701

N.d.-not detected. TON-turn over number is calculated as moles of reactant consumed per mole of catalyst. TOF-turn over frequency is calculated as moles of reactant consumed per mole of catalyst per unit time.

Table S3. Comparative result of catalysts in W/DMSO (1:4 ratio) at 170 °C 25% catalyst load on glucose after 180 min.

Catalysts	$Selectivity_{fru}$	$Selectivity_{HMF}$	$Yield_{LA}$ (%)	$Yield_{FA}$ (%)	TON_{HMF} (sec^{-1})	TOF_{HMF} (10^{-6})
Ta	10.67	80.49	n.d.	n.d.	0.0496	4.594
Ta-cal	12.59	71.55	n.d.	n.d.	0.0764	7.075
Nb	10.39	79.88	2.41	0.69	0.0667	6.177
Nb-cal	12.13	64.20	1.47	n.d.	0.0530	4.910
Ta/Nb-1.5	6.61	83.80	10.11	13.17	0.0339	3.143
Ta/Nb-2.5	6.64	86.55	9.83	6.39	0.0334	3.094
Ta/Nb-3.5	9.02	75.61	9.77	5.20	0.0336	3.115

N.d.-not detected. TON-turn over number is calculated as moles of reactant consumed per mole of catalyst. TOF-turn over frequency is calculated as moles of reactant consumed per mole of catalyst per unit time.

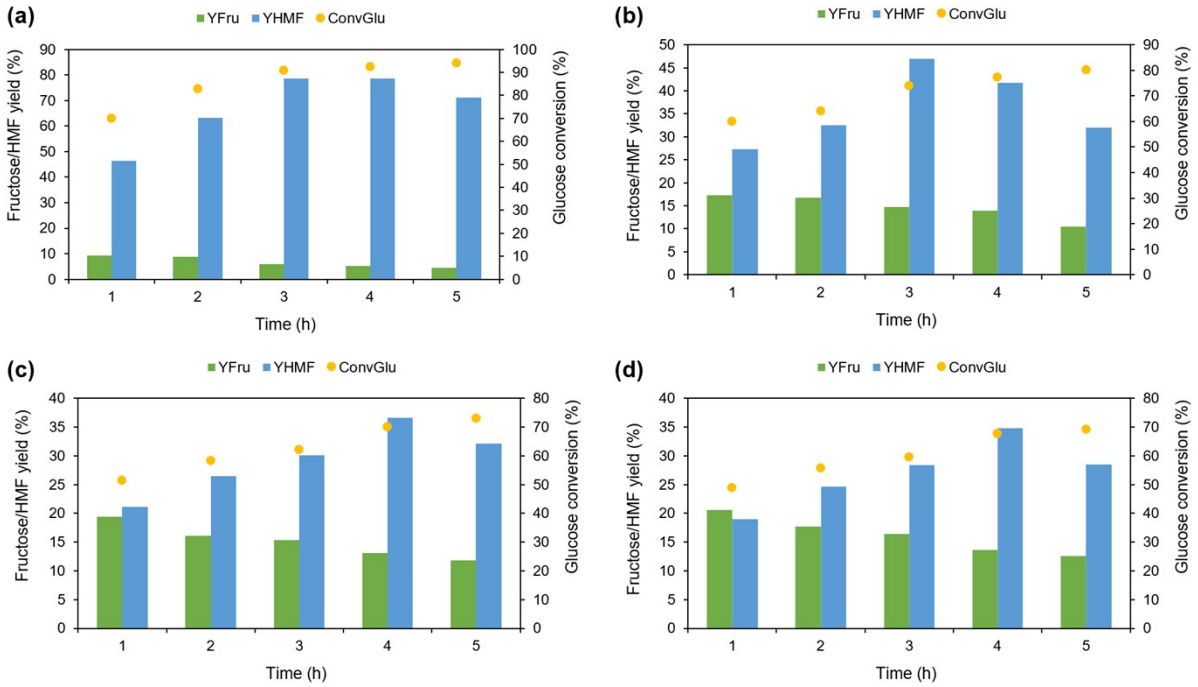

Figure S9. Glucose decomposition to HMF over Ta/Nb-2.5 catalyst in different aqueous-organic solvent mediums: (a) 1:4 vol. ratio W/DMSO, (b) 2:3 vol. ratio W/DMSO, (c) 3:2 vol. ratio W/DMSO, and (d) 4:1 vol. ratio W/DMSO. Reaction conditions: 170 °C and 25% wt. catalyst load for 5 h. YFru-yield fructose, YHMF-yield HMF and ConvGlu-glucose conversion.

Table S4. Dehydration result of glucose to 5-HMF over Ta/Nb-2.5 (25% on substrate) in W/DMSO (1:4) at 170 °C up to 300 min.

Time (min)	$Selectivity_{fru}$	$Selectivity_{HMF}$	$Yield_{LA}$ (%)	$Yield_{FA}$ (%)	TON_{HMF} (sec^{-1})	TOF_{HMF} (10^{-6})
60	13.39	66.31	0.91	n.d.	0.0226	6.285
120	10.78	76.31	2.76	2.29	0.0282	3.926
180	6.64	86.55	9.83	6.39	0.0334	3.094
240	5.63	85.07	10.38	10.70	0.0333	2.319
300	4.86	75.59	10.88	14.04	0.0309	1.718

TON-turn over number is calculated as moles of reactant consumed per mole of catalyst. TOF-turn over frequency is calculated as moles of reactant consumed per mole of catalyst per unit time.

Table S5. Dehydration result of glucose to 5-HMF over Ta/Nb-2.5 (25% on substrate) in W/DMSO (2:3) at 170 °C up to 300 min.

Time (min)	$Selectivity_{fru}$	$Selectivity_{HMF}$	$Yield_{LA}$ (%)	$Yield_{FA}$ (%)	TON_{HMF} (sec^{-1})	TOF_{HMF} (10^{-6})
60	28.96	45.68	0.54	n.d.	0.0151	4.194
120	26.23	50.83	2.51	2.29	0.0168	2.336
180	19.86	63.40	7.25	3.78	0.0216	2.002
240	17.99	53.97	9.90	6.40	0.0199	1.382
300	13.07	39.93	10.37	9.52	0.0166	0.925

TON-turn over number is calculated as moles of reactant consumed per mole of catalyst. TOF-turn over frequency is calculated as moles of reactant consumed per mole of catalyst per unit time.

Table S6. Dehydration result of glucose to 5-HMF over Ta/Nb-2.5 (25% on substrate) in W/DMSO (3:2) at 170 °C up to 300 min.

Time (min)	$Selectivity_{fru}$	$Selectivity_{HMF}$	$Yield_{LA}$ (%)	$Yield_{FA}$ (%)	TON_{HMF} (sec^{-1})	TOF_{HMF} (10^{-6})
60	37.72	41.04	n.d.	n.d.	0.0130	3.615
120	27.57	45.39	1.51	n.d.	0.0148	2.053
180	24.64	48.52	6.49	1.68	0.0160	1.484
240	18.72	52.15	9.39	4.24	0.0182	1.262
300	16.24	43.99	9.75	7.35	0.0167	0.9265

N.d.-not detected. TON-turn over number is calculated as moles of reactant consumed per mole of catalyst. TOF-turn over frequency is calculated as moles of reactant consumed per mole of catalyst per unit time.

Table S7. Dehydration result of glucose to 5-HMF over Ta/Nb-2.5 (25% on substrate) in W/DMSO (4:1) at 170 °C up to 300 min.

Time (min)	$Selectivity_{fru}$	$Selectivity_{HMF}$	$Yield_{LA}$ (%)	$Yield_{FA}$ (%)	TON_{HMF} (sec^{-1})	TOF_{HMF} (10^{-6})
60	41.94	38.76	n.d.	n.d.	0.0123	3.416
120	31.73	44.22	1.14	n.d.	0.0142	1.970
180	27.56	47.56	5.35	0.76	0.0154	1.429
240	20.15	51.43	8.70	5.11	0.0176	1.221
300	18.21	41.22	9.61	6.69	0.0155	0.860

N.d.-not detected. TON-turn over number is calculated as moles of reactant consumed per mole of catalyst. TOF-turn over frequency is calculated as moles of reactant consumed per mole of catalyst per unit time.

Table S8. Effect of catalyst loading on dehydration of glucose to 5-HMF at 170 °C in W/DMSO (1:4) using Ta/Nb-2.5 after 180 min.

Catalyst:substrate (wt.%)	$Selectivity_{fru}$	$Selectivity_{HMF}$	$Yield_{LA}$ (%)	$Yield_{FA}$ (%)	TON_{HMF} (sec^{-1})	TOF_{HMF} (10^{-6})
1:6	16.14	84.33	0.91	n.d.	0.0230	2.127
1:4	8.29	86.55	9.83	6.39	0.0334	3.094
1:2	7.58	56.33	13.39	8.50	0.0232	2.147

TON-turn over number is calculated as moles of reactant consumed per mole of catalyst. TOF-turn over frequency is calculated as moles of reactant consumed per mole of catalyst per unit time.

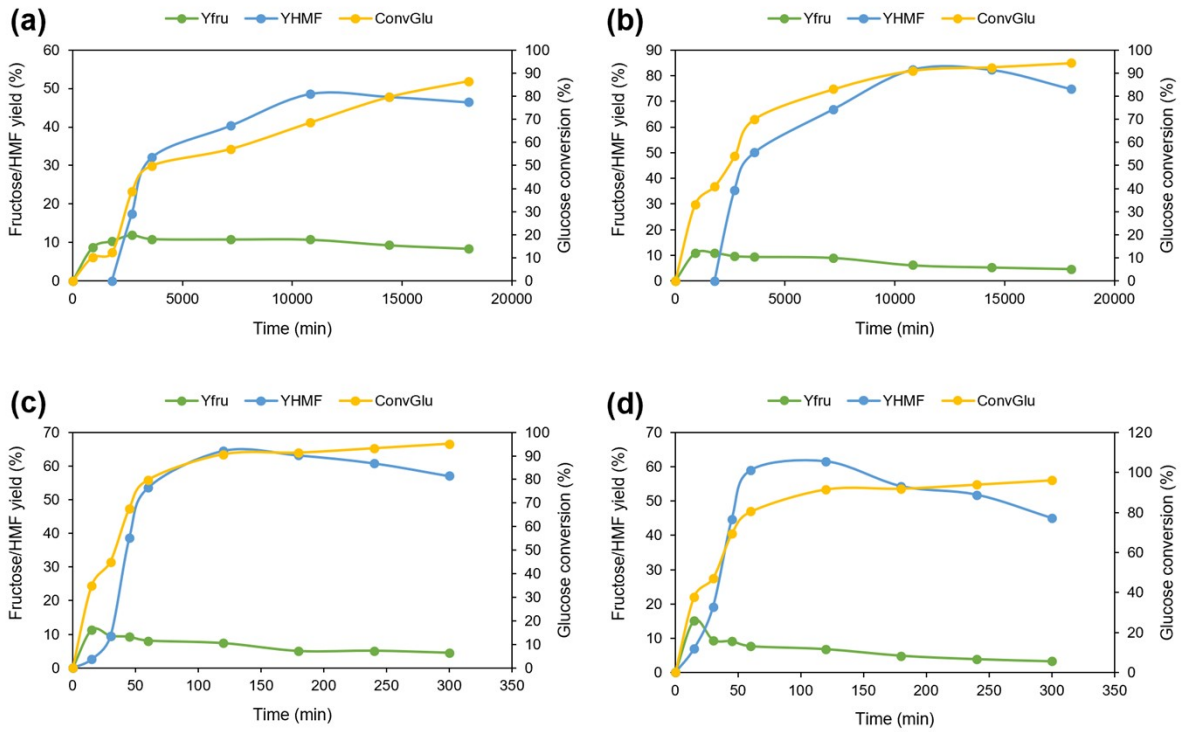

Figure S10. Glucose degradation and product(s) formation profile under different temperature conditions: (a) 160 °C, (b) 170 °C, (c) 180 °C, and (d) 190 °C. Reaction conditions: 1:4 vol. ratio W/DMSO medium and 25% wt. catalyst load (Ta/Nb-2.5) up to 5 h. Y-yield and Conv-conversion. YFru-yield fructose, YHMF-yield HMF and ConvGlu-glucose conversion.

Table S9. Effect of time on dehydration of glucose to 5-HMF at 160 °C in C in W/DMSO (1:4) using 25% of Ta/Nb-2.5 up to 300 min.

Time (min)	$Selectivity_{fru}$	$Selectivity_{HMF}$	$Yield_{LA}$ (%)	$Yield_{FA}$ (%)	TON_{HMF} (sec^{-1})	TOF_{HMF} (10^{-6})
15	84.08	n.d.	n.d.	n.d.	0	0
30	83.43	n.d.	n.d.	n.d.	0	0
45	30.70	44.82	n.d.	n.d.	0.0118	4.353
60	21.71	64.16	0.63	n.d.	0.0166	4.621
120	18.78	70.59	2.49	n.d.	0.0194	2.696
180	15.59	70.90	10.37	n.d.	0.0222	2.052
240	11.57	60.10	9.38	n.d.	0.0219	1.522
300	9.62	53.69	10.15	n.d.	0.0215	1.191

N.d.-not detected. TON-turn over number is calculated as moles of reactant consumed per mole of catalyst. TOF-turn over frequency is calculated as moles of reactant consumed per mole of catalyst per unit time.

Table S10. Effect of time on dehydration of glucose to 5-HMF at 170 °C in W/DMSO (1:4) using 25% of Ta/Nb-2.5 up to 300 min.

Time (min)	$Selectivity_{fru}$	$Selectivity_{HMF}$	$Yield_{LA}$ (%)	$Yield_{FA}$ (%)	TON_{HMF} (sec^{-1})	TOF_{HMF} (10^{-6})
15	32.84	n.d.	n.d.	n.d.	0	0
30	26.56	n.d.	n.d.	n.d.	0	0
45	17.88	65.36	n.d.	n.d.	0.0177	6.557
60	13.39	71.42	0.91	n.d.	0.0226	6.285
120	10.78	80.62	2.76	2.29	0.0283	3.926
180	6.64	90.48	9.83	6.39	0.0334	3.094
240	5.63	88.94	10.38	10.70	0.0334	2.319
300	4.86	79.39	10.88	14.04	0.0309	1.717

N.d.-not detected. TON-turn over number is calculated as moles of reactant consumed per mole of catalyst. TOF-turn over frequency is calculated as moles of reactant consumed per mole of catalyst per unit time.

Table S11. Effect of time on dehydration of glucose to 5-HMF at 180 °C in C in W/DMSO (1:4) using 25% of Ta/Nb-2.5 up to 300 min.

Time (min)	$Selectivity_{fru}$	$Selectivity_{HMF}$	$Yield_{LA}$ (%)	$Yield_{FA}$ (%)	TON_{HMF} (sec^{-1})	TOF_{HMF} (10^{-6})
15	32.60	7.51	n.d.	n.d.	0.0056	6.271
30	21.34	20.85	n.d.	n.d.	0.0091	5.058
45	13.83	57.02	1.49	n.d.	0.0188	6.978
60	10.27	67.11	4.00	n.d.	0.0239	6.628
120	8.21	71.15	8.55	n.d.	0.0275	3.822
180	5.59	69.16	13.06	1.00	0.0271	2.506
240	5.58	65.24	14.76	9.86	0.0263	1.825
300	4.81	59.94	16.16	19.86	0.0250	1.390

N.d.-not detected. TON-turn over number is calculated as moles of reactant consumed per mole of catalyst. TOF-turn over frequency is calculated as moles of reactant consumed per mole of catalyst per unit time.

Table S12. Effect of time on dehydration of glucose to 5-HMF at 190 °C in C in W/DMSO (1:4) using 25% of Ta/Nb-2.5 up to 300 min.

Time (min)	$Selectivity_{fru}$	$Selectivity_{HMF}$	$Yield_{LA}$ (%)	$Yield_{FA}$ (%)	TON_{HMF} (sec^{-1})	TOF_{HMF} (10^{-6})
15	39.96	18.56	n.d.	n.d.	0.0083	9.236
30	20.26	40.66	2.19	n.d.	0.0123	6.859
45	13.19	64.59	4.80	n.d.	0.0209	7.745
60	9.56	73.31	6.30	n.d.	0.0256	7.125
120	7.45	67.17	9.80	n.d.	0.0265	3.682
180	5.32	59.00	15.55	1.00	0.0241	2.230
240	4.14	55.12	18.04	13.25	0.0233	1.616
300	3.39	46.80	22.79	26.47	0.0210	1.166

N.d.-not detected. TON-turn over number is calculated as moles of reactant consumed per mole of catalyst. TOF-turn over frequency is calculated as moles of reactant consumed per mole of catalyst per unit time.

Table S13. Effect of temperature on dehydration of glucose to 5-HMF in W/DMSO (1:4) using 25% of Ta/Nb-2.5 after 180 min.

Temperature (°C)	$Selectivity_{fru}$	$Selectivity_{HMF}$	$Yield_{LA}$ (%)	$Yield_{FA}$ (%)	TON_{HMF} (sec^{-1})	TOF_{HMF} (10^{-6})	*Carbon balance (%)*
160	15.59	70.90	8.81	n.d.	0.0222	2.051	98.39
170	6.64	86.55	8.28	0.56	0.0334	3.094	98.69
180	5.59	69.16	13.83	0.78	0.0271	2.506	87.57
190	5.32	59.00	16.32	1.23	0.0241	2.230	82.22

N.d.-not detected. TON-turn over number is calculated as moles of reactant consumed per mole of catalyst. TOF-turn over frequency is calculated as moles of reactant consumed per mole of catalyst per unit time.

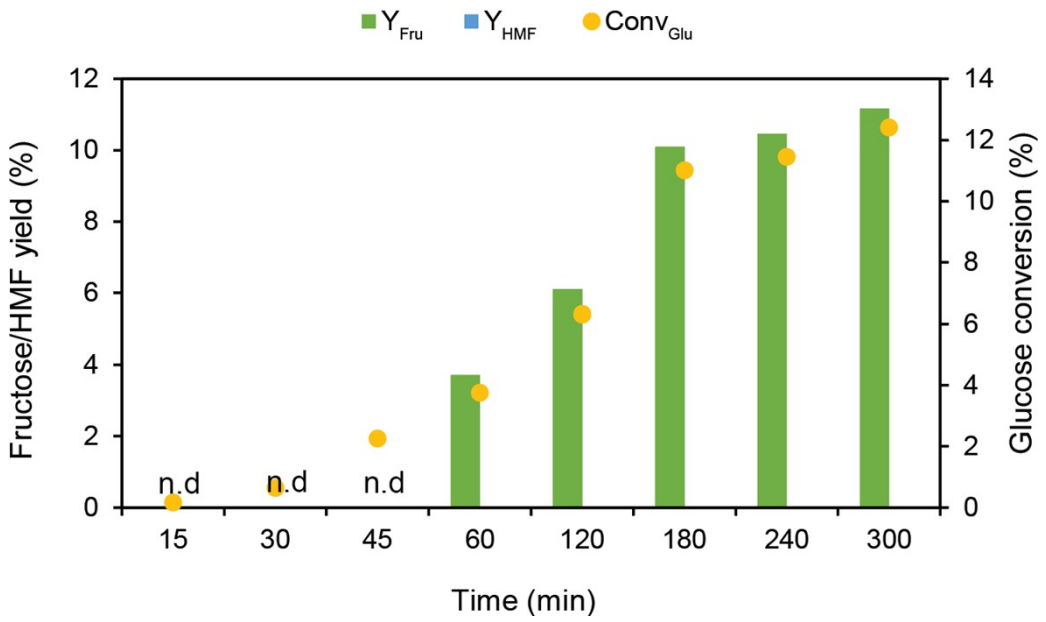

Figure S11. Glucose isomerization over Ta/Nb-2.5 catalyst in a water medium at 120 °C and 25% wt. catalyst load for 5 h. N.D.-not detected. YFru-yield fructose, YHMF-yield HMF and ConvGlu-glucose conversion.

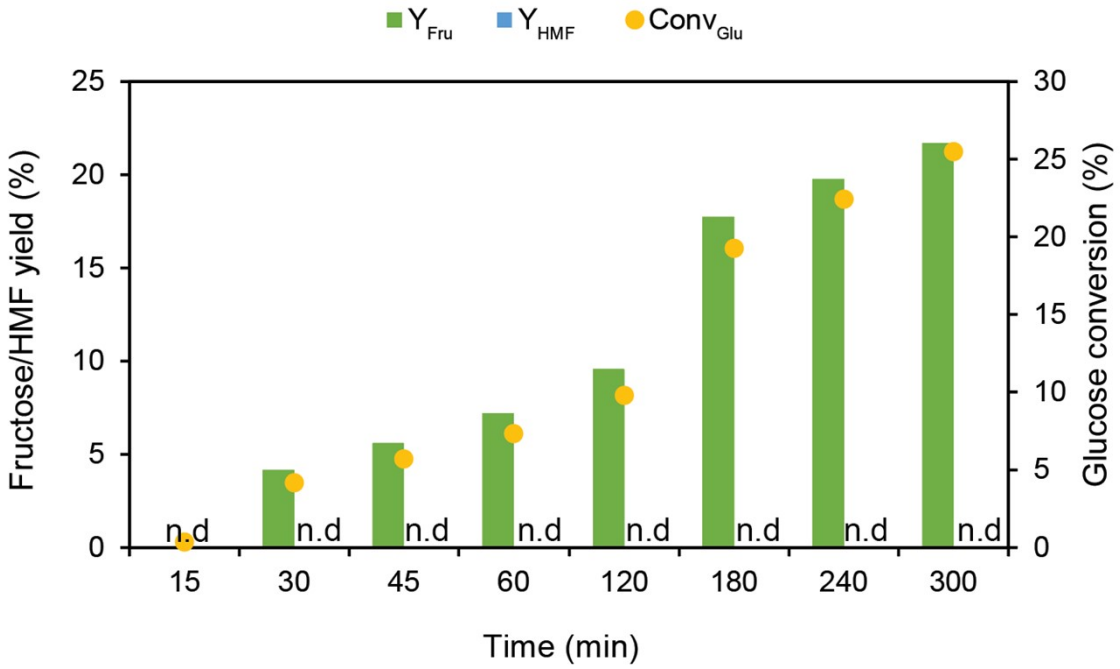

Figure S12. Glucose isomerization over Ta/Nb-2.5 catalyst in 1:4 vol. ratio W/DMSO at 120 °C and 25% wt. catalyst load for 5 h. N.D.-not detected. YFru-yield fructose, YHMF-yield HMF and ConvGlu-glucose conversion.

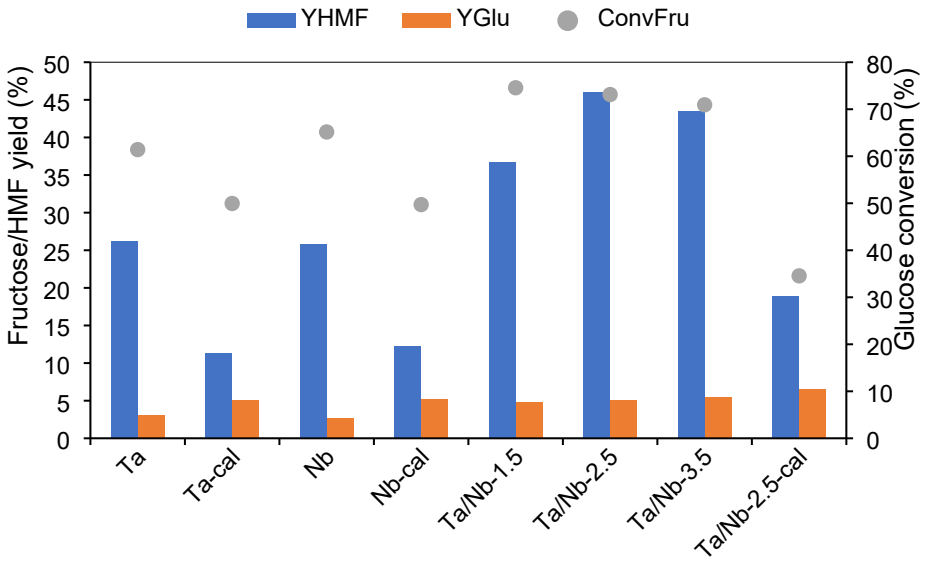

Figure S13. Catalyst's effectiveness on fructose decomposition to HMF in a water medium. Reaction conditions: 170 °C and 25% wt. catalyst load for 3 h. YHMF-yield HMF, YGlu-yield glucose and ConvFru-fructose conversion.

Table S14. Comparative result of catalysis in water at 170 °C using 25% catalyst load on substrate (fructose) after 180 min.

Catalysts	$Selectivity_{HMF}$	$Yield_{LA}$ (%)	$Yield_{FA}$ (%)	TON_{HMF} (sec^{-1})	TOF_{HMF} (10^{-6})
Ta	42.69	n.d.	n.d.	0.0268	2.485
Ta-cal	22.54	n.d.	n.d.	0.0337	3.126
Nb	39.56	n.d.	n.d.	0.0345	3.192
Nb-cal	24.63	n.d.	n.d.	0.0264	2.446
Ta/Nb-1.5	49.31	n.d.	n.d.	0.0177	1.637
Ta/Nb-2.5	62.91	n.d.	n.d.	0.0201	1.864
Ta/Nb-3.5	61.24	n.d.	n.d.	0.0208	1.927

N.d.-not detected. TON-turn over number is calculated as moles of reactant consumed per mole of catalyst. TOF-turn over frequency is calculated as moles of reactant consumed per mole of catalyst per unit time.

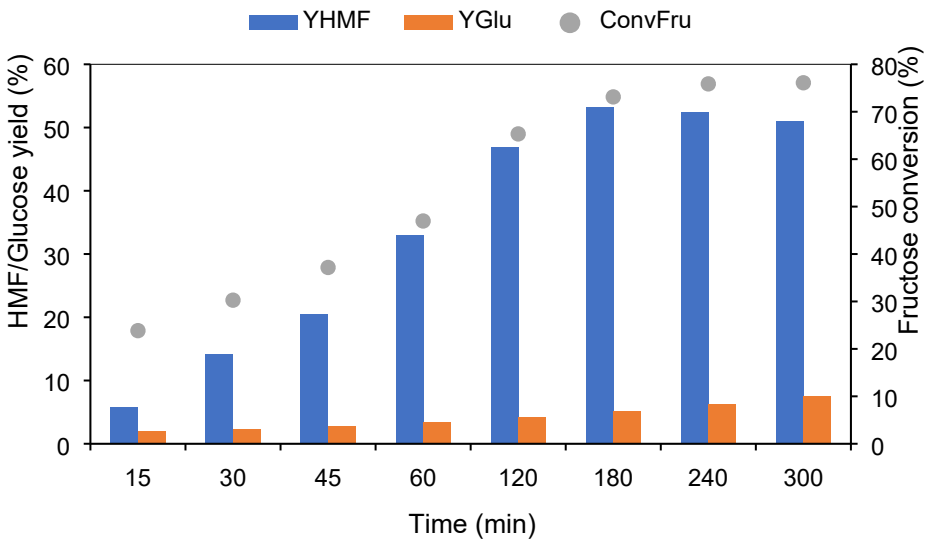

Figure S14. Time optimization of fructose decomposition to HMF in a water medium. Reaction conditions: 170 °C and 25% wt. catalyst load for 5 h. YHMF-yield HMF, YGlu-yield glucose and ConvFru-fructose conversion.

Table S15. Effect of time on dehydration of fructose to 5-HMF at 170 °C in a water medium using 25% of Ta/Nb-2.5 load on substrate up to 300 min.

Time (min)	$Selectivity_{HMF}$	$Yield_{LA}$ (%)	$Yield_{FA}$ (%)	TON_{HMF} (sec^{-1})	TOF_{HMF} (10^{-6})
15	23.92	n.d.	n.d.	0.0043	4.766
30	46.82	n.d.	n.d.	0.0071	3.954
45	55.12	n.d.	n.d.	0.0092	3.417
60	70.24	n.d.	n.d.	0.0134	3.722
120	71.71	n.d.	n.d.	0.0180	2.504
180	72.67	n.d.	n.d.	0.0201	1.864
240	69.11	n.d.	n.d.	0.0199	1.381
300	66.92	n.d.	n.d.	0.0194	1.077

N.d.-not detected. TON-turn over number is calculated as moles of reactant consumed per mole of catalyst. TOF-turn over frequency is calculated as moles of reactant consumed per mole of catalyst per unit time.

Table S16. Comparative result of catalysis in W/DMSO (1:4) at 170 °C using 25% catalyst load on substrate (fructose) after 180 min.

Catalysts	$Selectivity_{HMF}$	$Yield_{LA}$ (%)	$Yield_{FA}$ (%)	TON_{HMF} (sec^{-1})	TOF_{HMF} (10^{-6})
Ta	77.26	10.79	3.81	0.0843	7.810
Ta-cal	80.20	12.69	4.95	0.1626	15.068
Nb	86.06	8.76	3.54	0.1109	10.272
Nb-cal	82.59	11.79	4.11	0.1249	11.566
Ta/Nb-1.5	89.65	7.51	0.65	0.0459	4.250
Ta/Nb-2.5	92.30	6.12	1.25	0.0451	4.178
Ta/Nb-3.5	91.41	6.50	0.95	0.0484	4.481

N.d.-not detected. TON-turn over number is calculated as moles of reactant consumed per mole of catalyst. TOF-turn over frequency is calculated as moles of reactant consumed per mole of catalyst per unit time.

Table S17. Effect of time on dehydration of fructose to 5-HMF at 170 °C in W/DMSO (1:4) using 25% of Ta/Nb-2.5 load on substrate up to 300 min.

Time (min)	$Selectivity_{HMF}$	$Yield_{LA}$ (%)	$Yield_{FA}$ (%)	TON_{HMF} (sec^{-1})	TOF_{HMF} (10^{-6})	*Total carbon*
15	61.05	n.d.	n.d.	0.0328	36.446	92.31
30	78.93	n.d.	n.d.	0.0388	21.557	90.27
45	86.85	n.d.	n.d.	0.0421	15.581	93.52
60	89.12	n.d.	n.d.	0.0441	12.240	92.38
120	90.98	n.d.	n.d.	0.0447	6.206	93.68
180	92.30	6.12	1.25	0.0451	4.178	99.35
240	70.50	7.32	1.77	0.0378	2.628	85.21
300	62.34	7.94	1.82	0.0351	1.951	79.93

N.d.-not detected. TON-turn over number is calculated as moles of reactant consumed per mole of catalyst. TOF-turn over frequency is calculated as moles of reactant consumed per mole of catalyst per unit time.

Table S18. Effect of catalyst loading on dehydration of fructose to 5-HMF at 170 °C in W/DMSO (1:4) medium using Ta/Nb-2.5 load on substrate after 180 min.

Catalyst:substrate (wt.%)	$Selectivity_{HMF}$	$Yield_{LA}$ (%)	$Yield_{FA}$ (%)	TON_{HMF} (sec^{-1})	TOF_{HMF} (10^{-6})
1:6	82.79	n.d.	n.d.	0.0395	3.664
1:4	92.30	6.12	1.25	0.0451	4.178
1:2	76.83	7.73	1.45	0.0375	3.479

N.d.-not detected. TON-turn over number is calculated as moles of reactant consumed per mole of catalyst. TOF-turn over frequency is calculated as moles of reactant consumed per mole of catalyst per unit time.

Table S19. Effect of time on dehydration of fructose to 5-HMF at 160 °C in W/DMSO (1:4) medium using 25% of Ta/Nb-2.5 load on substrate up to 300 min.

Time (min)	$Selectivity_{HMF}$	$Yield_{LA}$ (%)	$Yield_{FA}$ (%)	TON_{HMF} (sec^{-1})	TOF_{HMF} (10^{-6})
15	58.69	n.d.	n.d.	0.0259	28.808
30	76.79	n.d.	n.d.	0.0341	18.952
45	78.31	n.d.	n.d.	0.0387	14.355
60	78.42	n.d.	n.d.	0.0394	10.950
120	78.43	n.d.	n.d.	0.0396	5.503
180	76.42	5.58	n.d.	0.0398	3.687
240	73.05	6.47	1.72	0.0387	2.687
300	68.26	7.58	1.77	0.0371	2.061

N.d.-not detected. TON-turn over number is calculated as moles of reactant consumed per mole of catalyst. TOF-turn over frequency is calculated as moles of reactant consumed per mole of catalyst per unit time.

Table S20. Effect of time on dehydration of fructose to 5-HMF at 180 °C in W/DMSO (1:4) medium using 25% of Ta/Nb-2.5 load on substrate up to 300 min.

Time (min)	$Selectivity_{HMF}$	$Yield_{LA}$ (%)	$Yield_{FA}$ (%)	TON_{HMF} (sec^{-1})	TOF_{HMF} (10^{-6})
15	74.71	3.26	0.00	0.0345	38.343
30	80.79	4.44	0.47	0.0395	21.957
45	81.10	5.98	0.56	0.0406	15.030
60	80.74	10.98	0.62	0.0413	11.463
120	79.60	12.84	1.24	0.0409	5.678
180	75.38	17.90	1.31	0.0395	3.655
240	64.17	21.14	6.49	0.0357	2.481
300	55.06	25.73	8.88	0.0327	1.816

N.d.-not detected. TON-turn over number is calculated as moles of reactant consumed per mole of catalyst. TOF-turn over frequency is calculated as moles of reactant consumed per mole of catalyst per unit time.

Table S21. Effect of time on dehydration of fructose to 5-HMF at 190 °C in W/DMSO (1:4) medium using 25% of Ta/Nb-2.5 load on substrate up to 300 min.

Time (min)	$Selectivity_{HMF}$	$Yield_{LA}$ (%)	$Yield_{FA}$ (%)	TON_{HMF} (sec^{-1})	TOF_{HMF} (10^{-6})
15	72.55	4.98	n.d.	0.0345	38.349
30	79.25	7.34	0.91	0.0396	22.009
45	79.87	9.83	1.02	0.0410	15.176
60	77.30	12.72	1.17	0.0401	11.144
120	71.25	18.84	1.21	0.0381	5.291
180	63.53	23.65	1.53	0.0355	3.289
240	56.39	25.92	6.96	0.0331	2.301
300	49.86	28.47	9.48	0.0310	1.720

N.d.-not detected. TON-turn over number is calculated as moles of reactant consumed per mole of catalyst. TOF-turn over frequency is calculated as moles of reactant consumed per mole of catalyst per unit time.

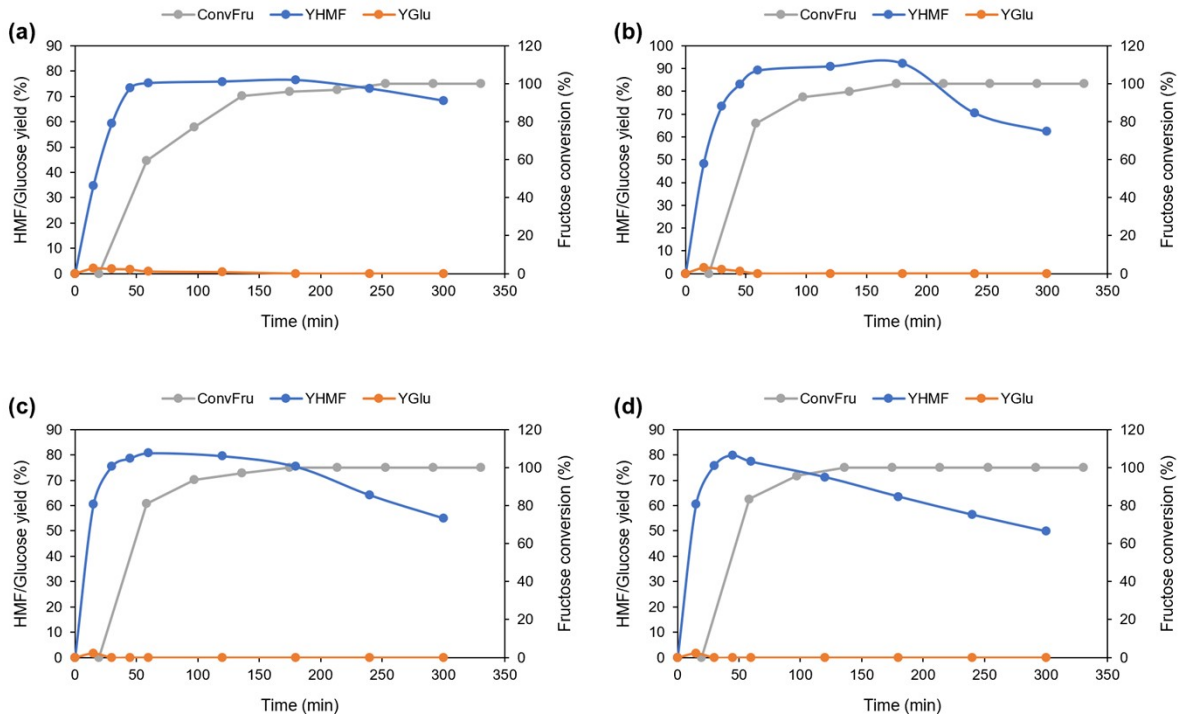

Figure S15. Glucose degradation and product(s) formation profile under different temperature conditions: (a) 160 °C, (b) 170 °C, (c) 180 °C, and (d) 190 °C. Reaction conditions: 1:4 vol. ratio W/DMSO medium and 25% wt. catalyst load up to 5 h. Y-yield and Conv-conversion.

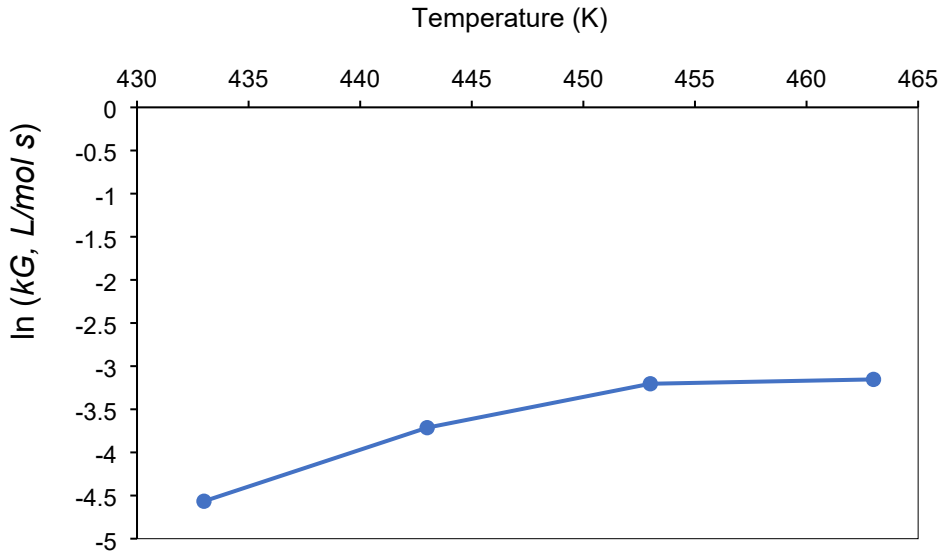

Figure S16. Correlation plot of temperature vs. second-order kinetics of glucose decomposition over Ta/Nb-2.5 catalyst in 1:4 vol. ratio W/DMSO under different temperature conditions (160-190 °C) at 25% wt. catalyst load up to 5 h.

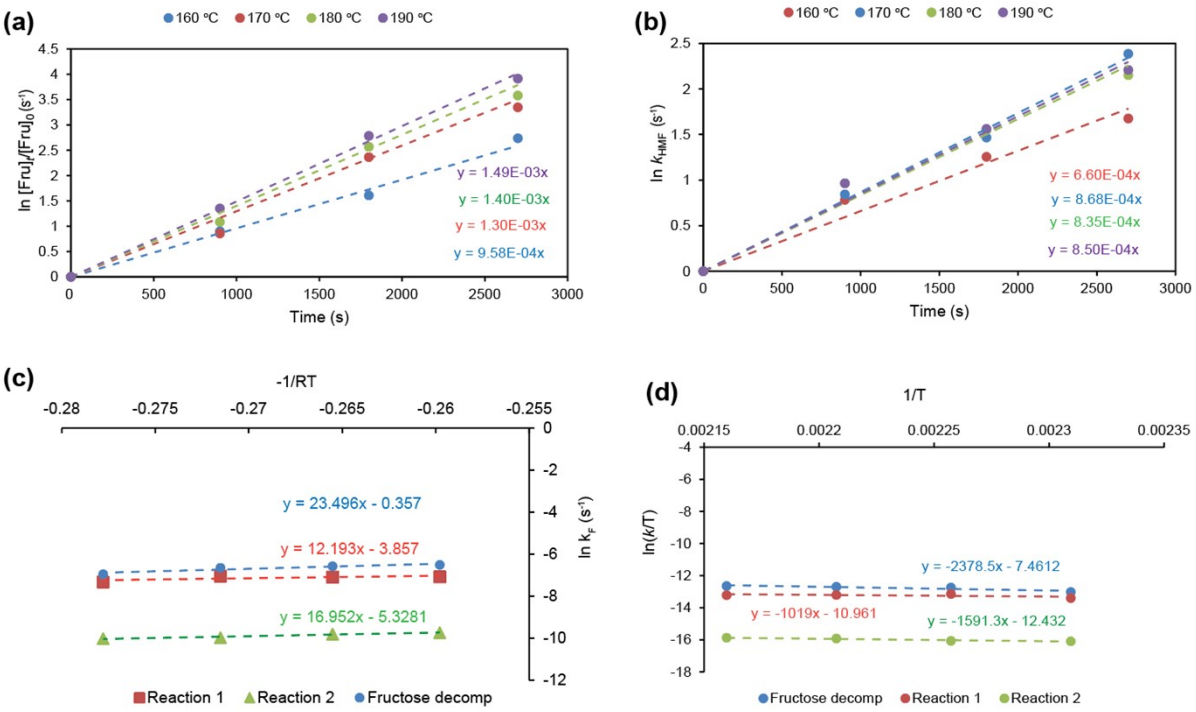

Figure S17. (a) First-order kinetics of fructose decomposition over Ta/Nb-2.5 catalyst in 1:4 vol. ratio W/DMSO under different temperature conditions (160-190 °C) at 25% wt. catalyst load up to 5 h; (b) first-order kinetics of HMF formation over Ta/Nb-2.5 catalyst in 1:4 vol. ratio W/DMSO under different temperature conditions (160-190 °C) at 25% wt. catalyst load up to 5 h; (c) Arrhenius plot of rate kinetics of fructose decomposition and reactions (1&2) *vs.* temperature (160-190 °C) over Ta/Nb-2.5 catalyst in 1:4 vol. ratio W/DMSO; (d) Eyring plot of rate kinetics of fructose decomposition and reactions (1&2) *vs.* temperature (160-190 °C) over Ta/Nb-2.5 catalyst in 1:4 vol. ratio W/DMSO.

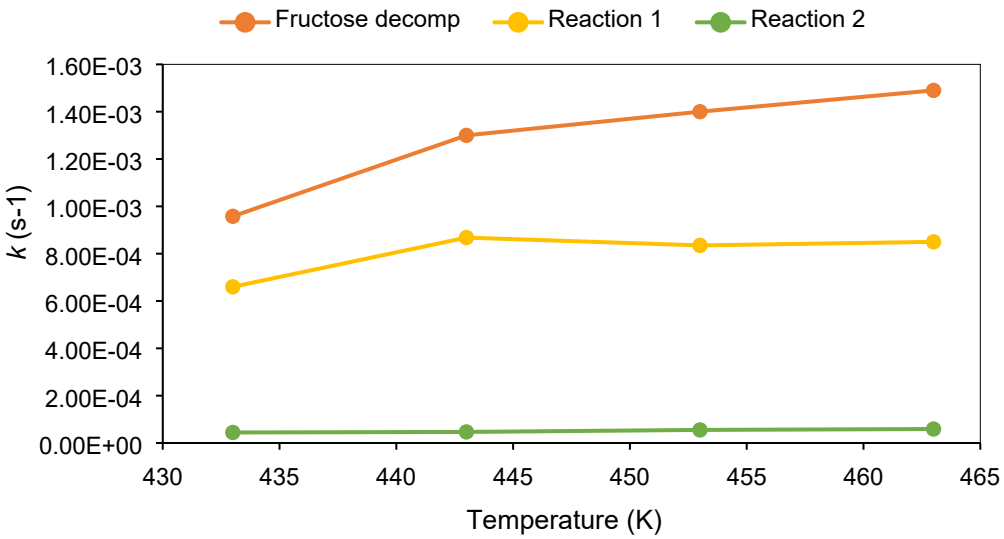

Figure S18. Correlation plot of temperature vs. kinetic rate constants of fructose decomposition and reactions (1&2) over Ta/Nb-2.5 catalyst in 1:4 vol. ratio W/DMSO under different temperature conditions (160-190 °C) at 25% wt. catalyst load up to 5 h.

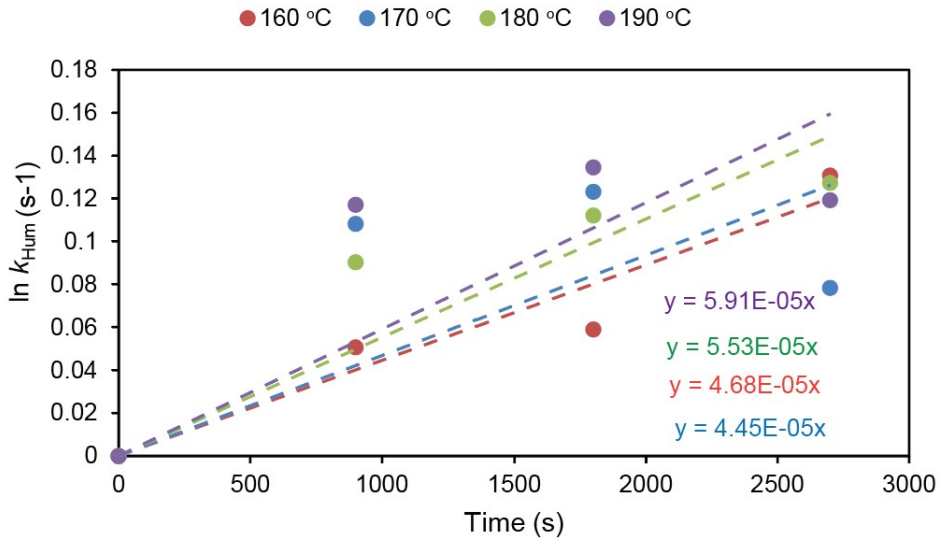

Figure S19. First-order rate kinetics of reaction 2 (humin formation) over Ta/Nb-2.5 catalyst in 1:4 vol. ratio W/DMSO under different temperature conditions (160-190 °C) at 25% wt. catalyst load up to 5 h.

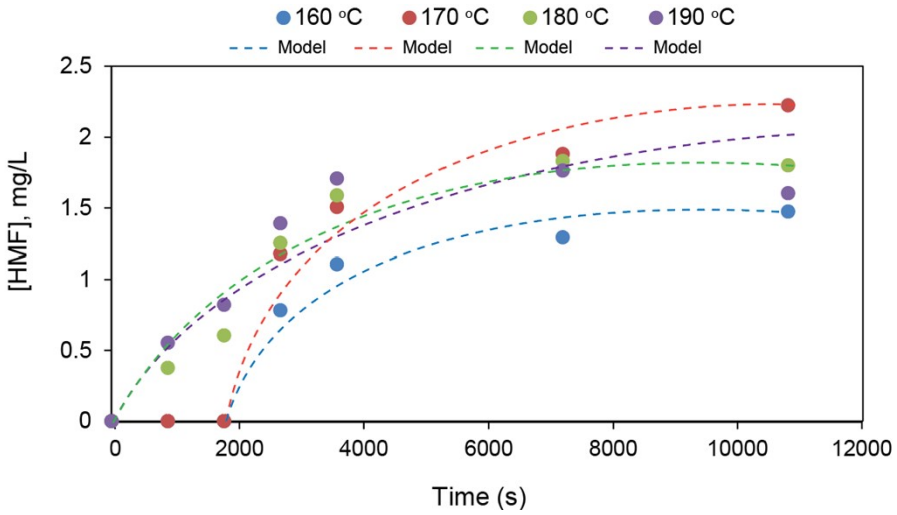

Figure S20. Results of experimental vs. model predicted HMF formation over Ta/Nb-2.5 catalyst in 1:4 vol. ratio W/DMSO under different temperature conditions (160-190 °C) at 25% wt. catalyst load up to 5 h.

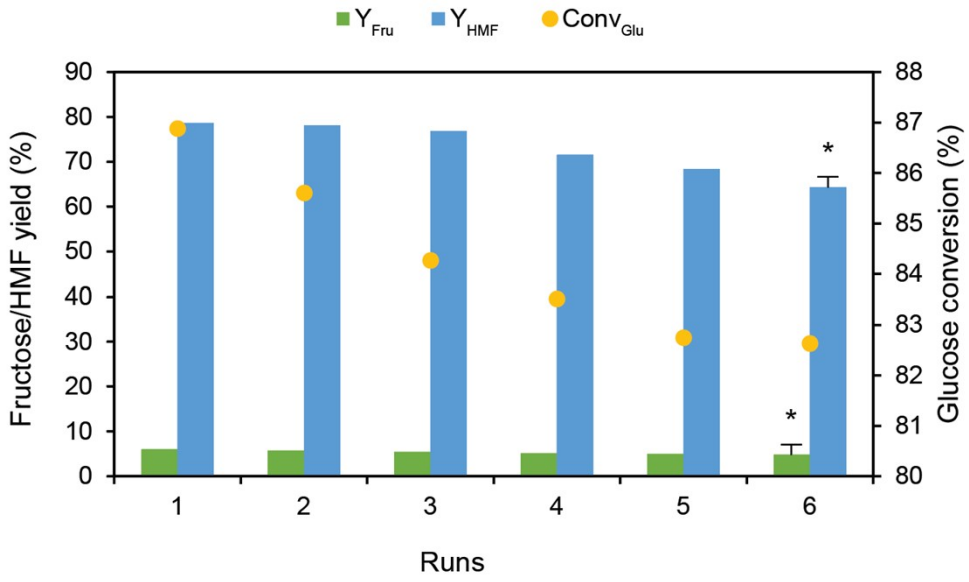

Figure S21. Result of Ta/Nb-2.5 recyclability in glucose dehydration to 5-HMF at 170 °C in W/DMSO (1:4) medium using 25% of Ta/Nb-2.5 on substrate after 180 min. YFru-yield fructose, YHMF-yield HMF and ConvGlu-glucose conversion. Error bar represent the standard error. The asterisk marks (* and **) denote the mean data significance and non-significance through ANOVA analysis at α=0.05.

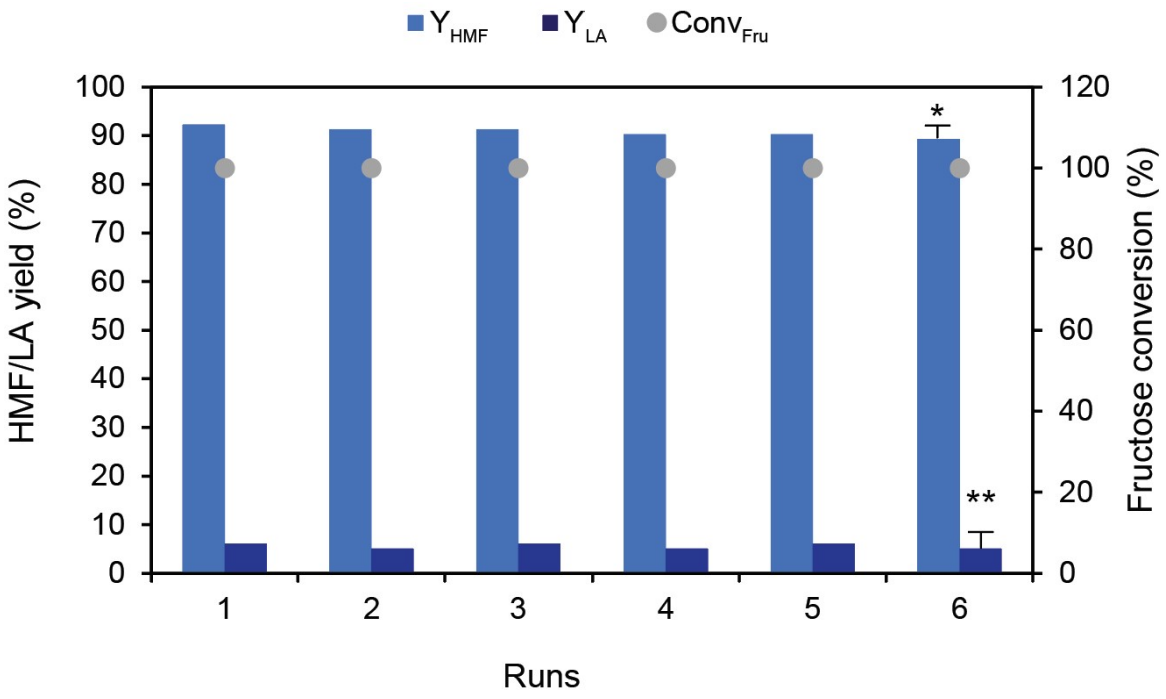

Figure S22. Result of Ta/Nb-2.5 recyclability in fructose dehydration to 5-HMF at 170 °C in W/DMSO (1:4) medium using 25% of Ta/Nb-2.5 on substrate after 180 min. YFru-yield fructose, YHMF-yield HMF and ConvGlu-glucose conversion. Error bar represent the standard error. The asterisk marks (* and **) denote the mean data significance and non-significance through ANOVA analysis at α=0.05.

Table S22. Result of Ta/Nb-2.5 recyclability in glucose dehydration to 5-HMF at 170 °C in W/DMSO (1:4) medium using 25% of Ta/Nb-2.5 on substrate after 180 min.

Cycle	$Selectivity_{fru}$	$Selectivity_{HMF}$	$Yield_{LA}$ (%)	$Yield_{FA}$ (%)
Fresh	6.64	86.55	8.83	6.39
1	6.14	86.01	7.73	4.11
2	5.64	85.91	7.68	4.04
3	5.68	84.25	7.52	3.96
4	6.25	84.85	7.26	3.90
5	5.02	80.51	7.84	4.14

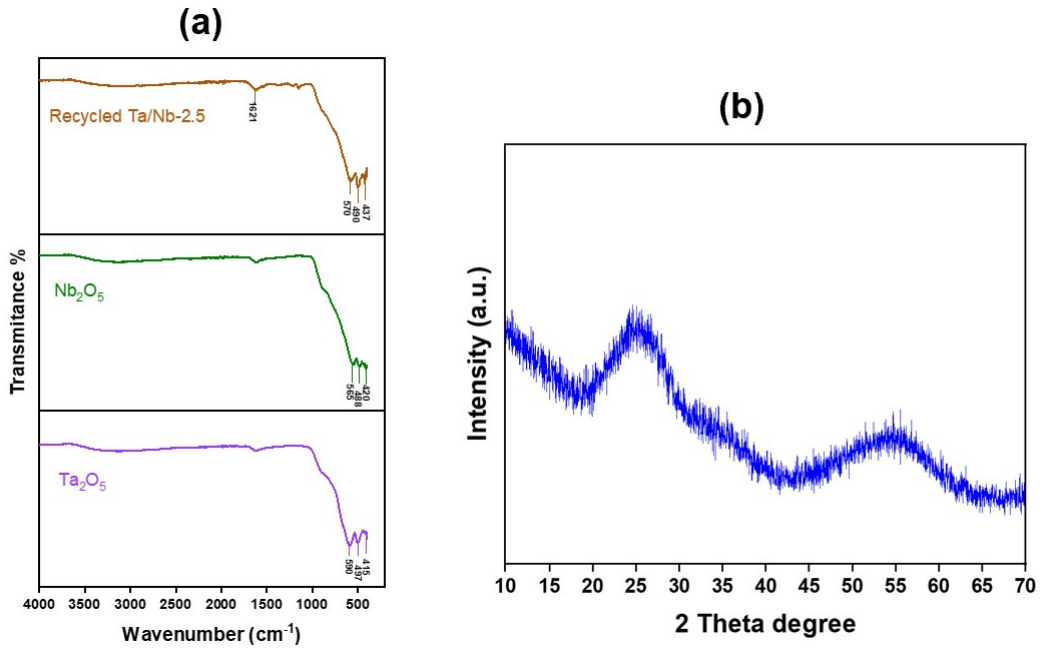

Figure S23. FTIR and XRD reports of the recycled Ta/Nb-2.5 catalyst after 6 runs (including the fresh run under optimum conditions).

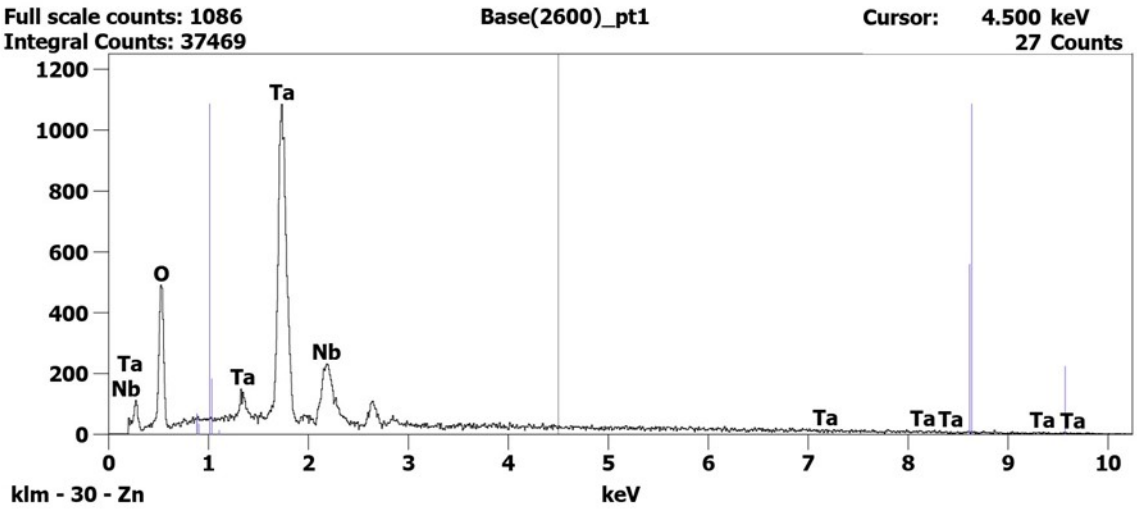

Figure S24. EDX result of the recycled Ta/Nb-2.5 catalyst after 6 runs (under optimum conditions).

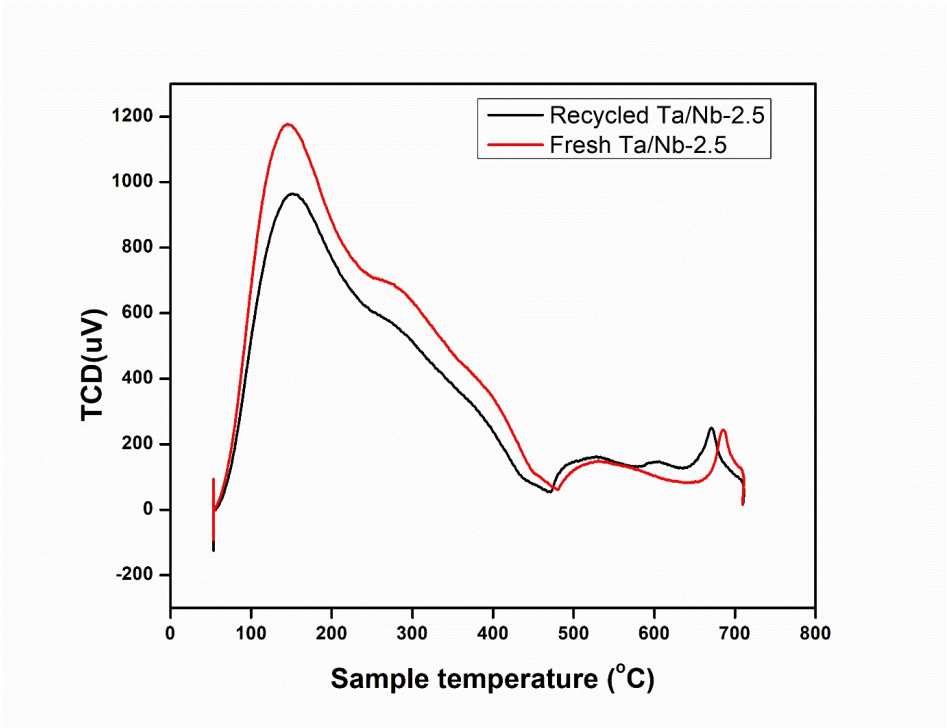

Figure S25. Comparative TPD result of recycled Ta/Nb-2.5 catalyst after 6 runs (under optimum conditions) and fresh Ta/Nb-2.5 catalyst.

Table S23. Comparative result of metal oxide catalysis of glucose to HMF.

Substrate	Catalyst	Reaction conditions	$Yield_{HMF}$ %	$Selectivity_{HMF}$ %	Ref.
Glucose	Nb/ZrO_2	H_2O, 3 h, 180 ◦C	22	Not mentioned	1
Glucose	NbO/NbP	H_2O, 2 h, 152 ◦C	26.5	56	2
Glucose	Al_2O_3-B_2O_3	DMSO, 2 h 140 °C	41.4	Not mentioned	3
Glucose	SO_4^{2-}/ZrO^{2-} Al_2O_3	DMSO, 4 h, 130 °C	48.0	Not mentioned	4
Glucose	Sn doped Ta_2O_5	Water/DMSO, 4h, 180 °C	57	80	5
Glucose	SO_4^{2-}/TiO_2-SiO_2	Water/DMSO, 12 h,140 °C	37	Not mentioned	6
Glucose	$Na_2ZrSi_4O_{11}$ + Amberlyst-15	THF-water, 1.5 h, 180 °C	39	Not mentioned	7
Glucose	Ion exchange resin-Alumina	Water-NMP medium at 120 °C for 8 h	84.9	90.4	8
Glucose	**Ta_2O_5/Nb_2O_5**	**Water/DMSO, 3 h, 170 °C**	**78.6**	**86.5**	**This work**

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