Supplementary Information (SI) for Green Chemistry.
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Improving both activity and stability for direct conversion of cellulose to ethanol by decorating Pt/WO_x with mononuclear NbO_x

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Table S1 Physicochemical properties of WO_x supported catalysts.

Sample	S_{BET} m^2/g	Average pore diameter nm	Total pore volume (cm^3/g)	E_g [a] (eV)
0.5Pt/WO_x	65.3	7.6	0.12	2.73
0.1Nb/0.5Pt/WO_x	66.8	9.8	0.16	2.52
0.1Ta/0.5Pt/WO_x	59.6	10.3	0.15	2.68
0.1Mo/0.5Pt/WO_x	62.2	10.5	0.16	2.61

[a] The electronic edge values of various WO_x based samples were determined by UV-vis DRS spectra.

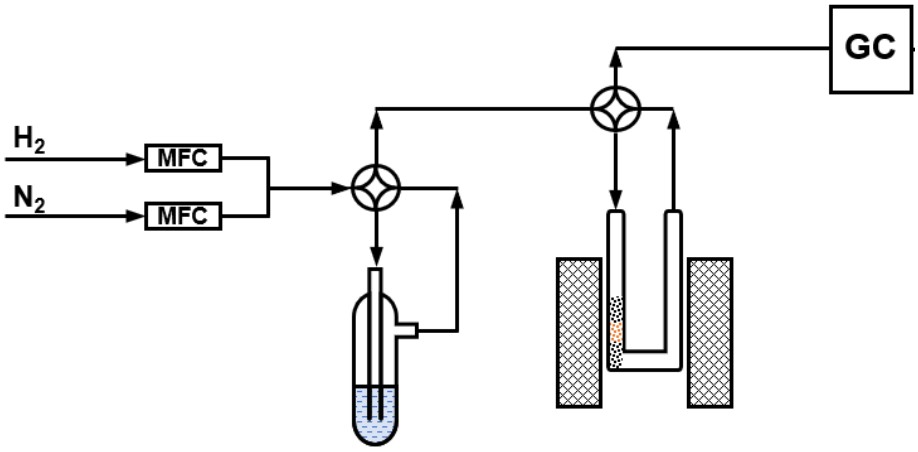

Figure S1 Schematic diagram of 2-butanol dehydration/dehydrogenation experiments

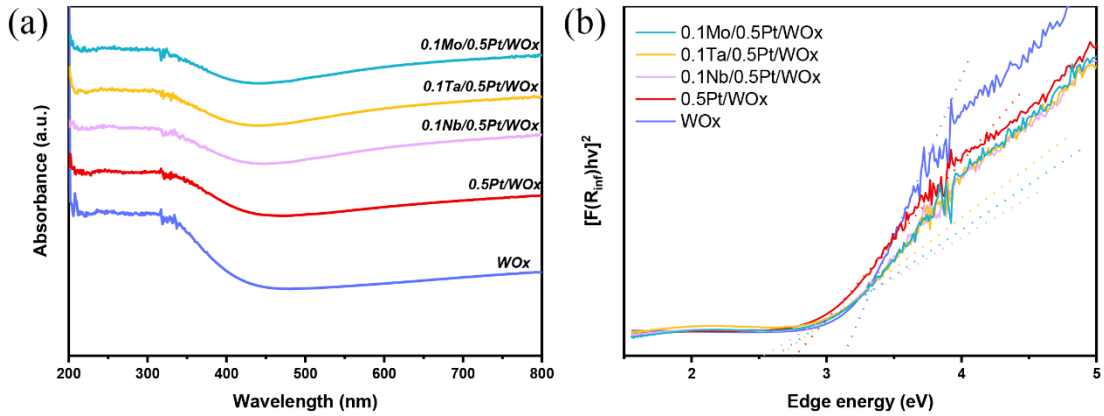

Figure S2 UV-vis DRS spectra (a) and edge energy (b) of the various WO_x based catalysts.

Table S2 The hydrogenolysis of EG over various catalysts

Catalyst	Conversion (%)	Ethanol selectivity (%)
$0.5Pt/WO_x$	6.7	40.6
$0.1Mo/0.5Pt/WO_x$	10.2	66.9
$0.1Nb/0.5Pt/WO_x$	16.4	80.4
$0.1Ta/0.5Pt/WO_x$	11.5	70.2

Reaction conditions:0.1 g catalyst, 0.1 g ethylene glycol, 9.9 g H_2O, 180 ^oC, 4.0 MPa H_2, 2 h, 700 rpm.

Table S3 The effect of Ta and Fe loadings on the catalytic performance for the one pot conversion of cellulose.

Entry	Catalyst	Carbon yield (%)					
		EG	Ethanol	1,2-PG	Propanol	Butanol	TOC
1	0.5Pt/WO_x	15.2	17.7	1.6	5.7	3.3	67.0
2	0.05Ta/0.5Pt/WO_x	20.2	18.3	1.9	1.1	5.8	74.5
3	0.1Ta/0.5Pt/WO_x	24.8	22.0	4.3	3.2	3.4	79.1
4	0.2Ta/0.5Pt/WO_x	18.5	18.2	1.3	1.6	5.5	73.6
5	0.05Fe/0.5Pt/WO_x	21.9	20.0	2.5	1.6	6.1	77.4
6	0.1Fe/0.5Pt/WO_x	12.4	22.4	1.5	7.0	3.6	78.1
7	0.2Fe/0.5Pt/WO_x	29.1	14.9	2.0	1.3	7.7	75.4

Reaction conditions: 0.1 g catalyst, 0.1 g cellulose, 9.9 g H_2O, 245 ^oC, 6.0 MPa H_2, 2 h, 700 rpm. Under the reaction conditions, the cellulose was completely converted with all of the investigated catalysts. 1,2-PG stands for 1,2-propanediol.

Table S4 The comparison of ethanol formation rate over various catalysts.

No	Catalyst	Formation rate $g_{ethanol} \cdot g_{metal}^{-1} \cdot h^{-1}$	Ref
1	5Ru-25WO_x/HZSM-5+ 5Ru/WO_x	0.34	[1]
2	2Ir-20WO_x/SiO_2	1.56	[2]
2	5Pt/WO_x+5Pt@HZSM-5	2.09	[3]
3	2Pt/ZrO_2+H_2WO_4	4.91	[4]
4	2Pd-20Cu-30WO_x/SiO_2	8.16	[5]
5	0.1Mo/2Pt/WO_x	12.44	[6]
6	**0.1Nb/0.5Pt/WO_x**	**25.90**	**This work**

Ethanol formation rate: (Ethanol content (mol)×yield×46.07)/(reaction time× amounts of catalyst ×precious metal loading).

Notes and references

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Table S5 The catalytic performance of Pt/WO_x for the one-pot conversion of cellulose

Entry	Catalyst	Carbon yield (%)					
		EG	Ethanol	1,2-PG	Propanol	Butanol	TOC
1	WO_x	1.4	0	1.0	1.6	1.5	63.2
2	$0.05Pt/WO_x$	10.0	10.3	1.2	9.0	2.7	81.1
3	$0.1Pt/WO_x$	9.8	13.3	1.2	5.7	3.2	70.3
4	$0.25Pt/WO_x$	9.8	15.3	0.9	8.3	2.7	64.8
5	$0.5Pt/WO_x$	15.2	17.7	1.6	5.7	3.3	67.0
6	$1.0Pt/WO_x$	10.9	18.4	1.0	6.5	3.5	51.4
7	$2.0Pt/WO_x$	4.9	20.3	1.9	5.7	2.4	55.5
8	$4.0Pt/WO_x$	0.5	20.8	0	4.6	0	41.4

Reaction conditions: 0.1 g catalyst, 0.1 g cellulose, 9.9 g H_2O, 245 ^oC, 6.0 MPa H_2, 2 h, 700 rpm. Under the reaction conditions, the cellulose was completely converted with all of the investigated catalysts. 1,2-PG stands for 1,2-propanediol.

Table S6 The one-pot conversion of cellulose over various supported Pt catalysts

Entry	Catalyst	Carbon yield (%)					
		EG	Ethanol	1,2-PG	Propanol	Butanol	TOC
1	0.5Pt/WO_x	15.2	17.7	1.6	5.7	3.3	67.0
2	0.5Pt/Nb_2O_5	3.7	8.2	3.1	4.9	4.0	53.8
3	0.5Pt/Ta_2O_5	4.4	2.4	0.8	7.0	4.6	52.9
4	0.5Pt/MoO_3	3.3	5.3	6.0	7.4	4.8	60.8

Reaction conditions:0.1 g catalyst, 0.1 g cellulose, 9.9 g H_2O, 245 ^oC, 6.0 MPa H_2, 2 h. Under the reaction conditions, the cellulose was completely converted with all of the investigated catalysts. 1,2-PG stands for 1,2-propanediol.

Table S7 The effect of cellulose concentration over 0.1Nb/0.5Pt/WO_x catalyst

Cellulose Concentration (wt.%)	Carbon yield (%)					
	EG	Ethanol	1,2-PG	Propanol	Butanol	TOC
1	21.8	33.7	3.2	5.5	4.9	73.1
2	11.0	28.3	2.4	7.2	5.2	71.1
5	7.8	21.3	2.7	10.1	5.8	56.6
10 [a]	5.7	17.1	0.6	5.5	3.2	47.2

Reaction conditions: 0.1 g catalyst ([a]: 0.5 g catalyst), cellulose + H_2O = 10.0 g, 245 °C, 6.0 MPa H_2, 2 h, 700 rpm. TOC means total organic carbon in the liquid product. Under the reaction conditions, the cellulose was completely converted with all of the investigated catalysts. 1,2-PG stands for 1,2-propanediol.

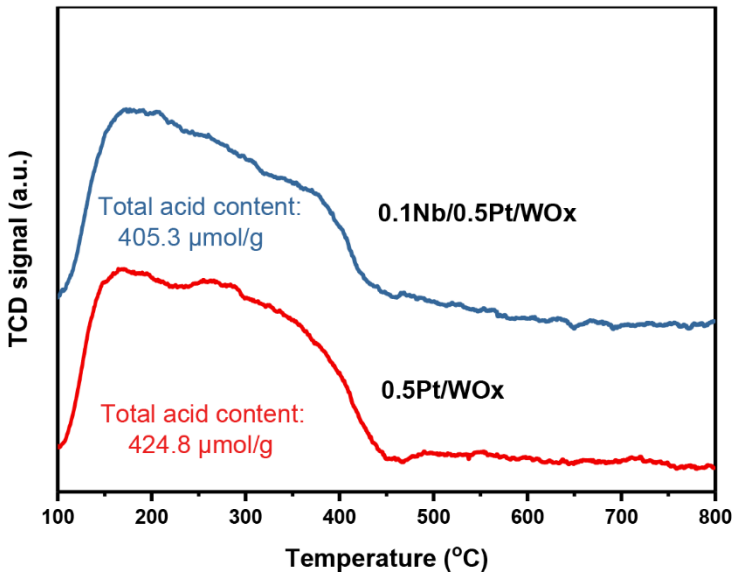

Figure S3 The NH_3-TPD profiles of $0.5Pt/WO_x$ and $0.1Nb/0.5Pt/WO_x$ samples.

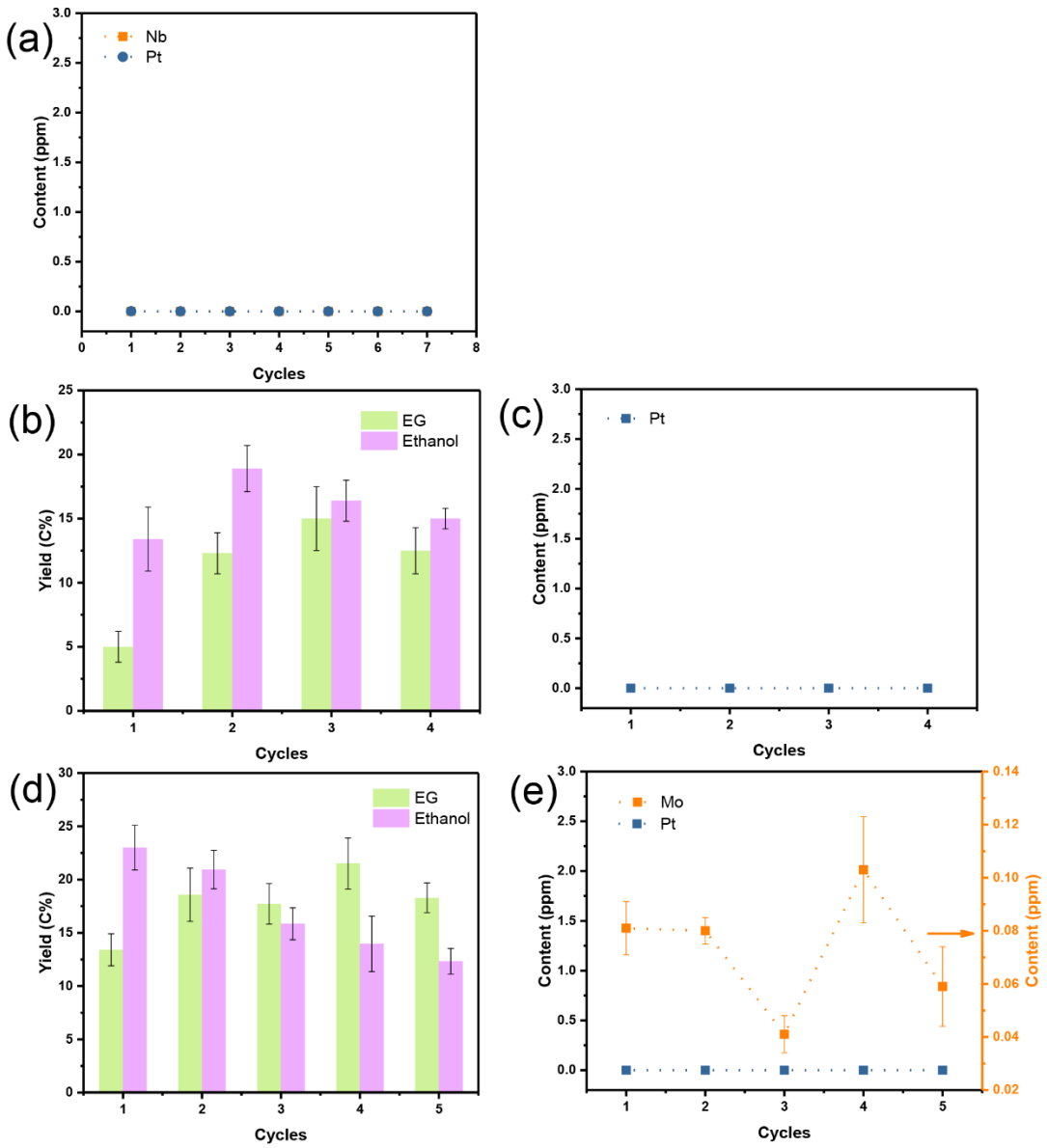

Figure S4 The corresponding metal concentrations in liquid after each cycle determined by ICP-OES for 0.1Nb0.5Pt/WO_x (a). The stability tests for the catalytic conversion of cellulose over 0.5Pt/WO_x(b), 0.1Mo/0.5Pt/WO_x (d) and corresponding metal concentrations in liquid after each cycle determined by ICP-OES (c, e). Reaction conditions: 0.1 g cellulose, 0.1 g catalyst, 9.9 g H_2O, 245 °C, 6.0 MPa, 2 h, 700 rpm. Under the reaction conditions, the cellulose was completely converted with all of the investigated catalysts.

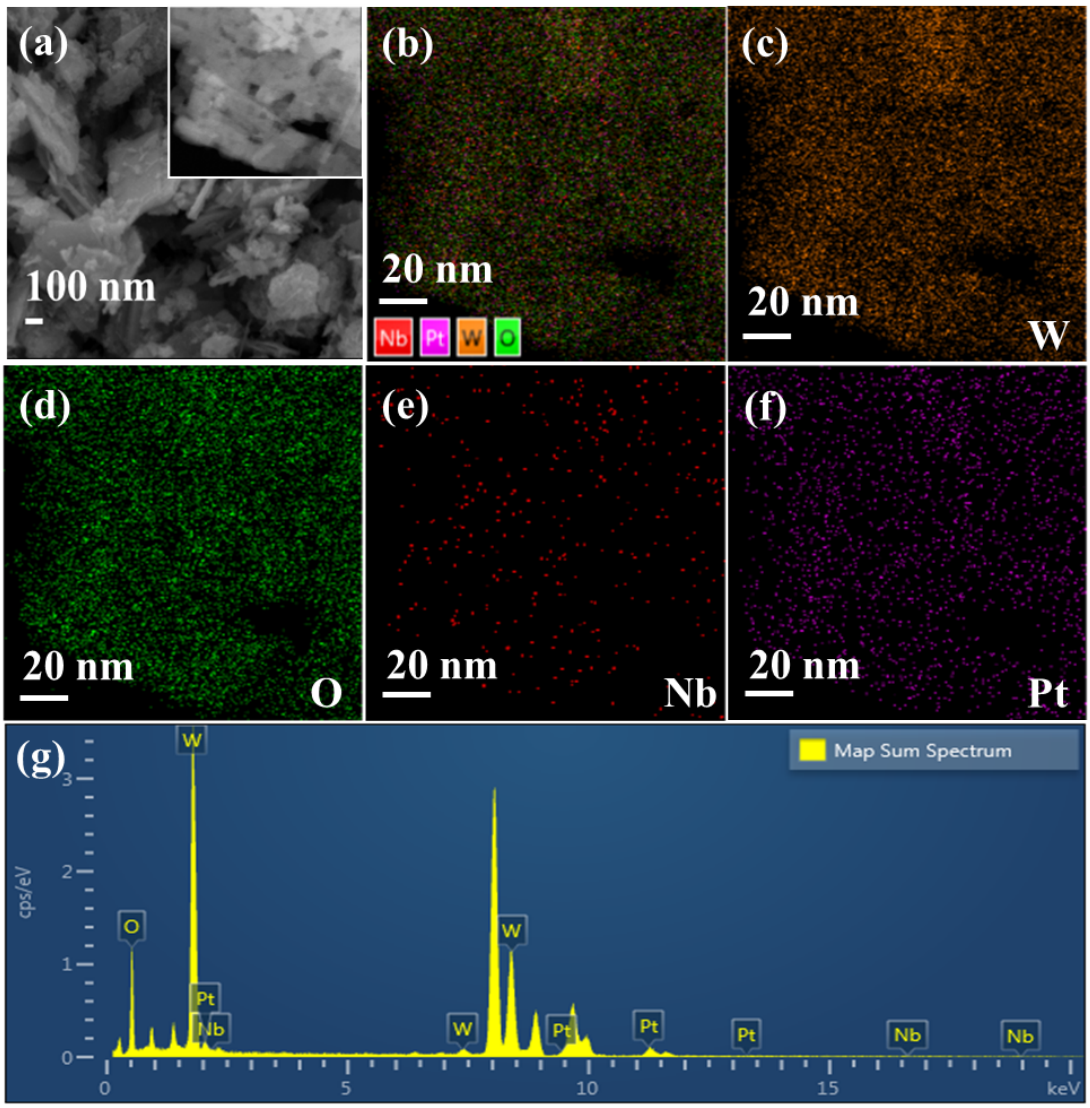

Figure S5 The SEM image (a), HAADF-STEM images of spent 0.1Nb/0.5Pt/WO_x (inset image of (a)) and corresponding elemental maps (b-f), and the EDX spectrum (g).