Supporting Information

Green Chemistry

Highly Active Niobium-Loaded Montmorillonite Catalysts for the Production of 5-Hydroxymethylfurfural from Glucose

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Table S1 The original data about chemical composition (wt%) of Nb-MMT from XRF

Catalyst	SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3	K_2O	Na_2O	P_2O_5	Nb_2O_5
MMT	73.99	13.95	5.82	3.00	1.72	1.20	0.25	0.07	0.00
0.25Nb-MMT	73.74	14.18	5.34	3.08	1.75	1.24	0.23	0.06	0.37
0.5Nb-MMT	74.39	13.95	4.54	3.04	1.70	1.23	0.30	0.08	0.78
1Nb-MMT	74.43	14.28	3.56	2.82	1.79	1.27	0.23	0.07	1.56
2Nb-MMT	74.78	13.89	2.24	2.84	1.66	1.19	0.23	0.05	3.12
3Nb-MMT	73.63	13.79	2.07	2.67	1.72	1.32	0.23	0.08	4.50
1Nb-MMT-500	75.02	13.66	3.18	2.73	1.71	1.22	0.27	0.04	2.17
1Nb-MMT-900	74.05	14.15	2.99	2.85	1.73	1.28	0.26	0.06	2.64

Table S2 Elemental content (wt%) of Nb-MMT determined by XRF

Catalyst	Si	Al	Ca	Mg	Fe	K	Na	P	Nb
MMT	34.53	7.38	4.16	1.80	1.20	1.00	0.18	0.03	0.00
0.25Nb-MMT	34.41	7.51	3.82	1.85	1.22	1.03	0.17	0.03	0.26
0.5Nb-MMT	34.71	7.38	3.24	1.83	1.19	1.02	0.22	0.03	0.54
1Nb-MMT	34.73	7.56	2.54	1.69	1.25	1.05	0.17	0.03	1.09
2Nb-MMT	34.90	7.35	1.60	1.70	1.16	0.99	0.17	0.02	2.18
3Nb-MMT	34.36	7.30	1.48	1.60	1.20	1.09	0.17	0.03	3.15
1Nb-MMT-500	35.01	7.23	2.27	1.64	1.20	1.02	0.20	0.02	1.52
1Nb-MMT-900	34.56	7.49	2.13	1.71	1.21	1.06	0.19	0.03	1.85

Table S3 Overview of glucose conversion to 5-HMF yield using various niobium-containing catalysts under optimal conditions [a]

Entry	Catalyst	Experimental parameter		Ref
		Conversion/%	Yield/%	
1	Nb_2O_5/H_3PO_4	92.0	52.0	S1
2	Nb_x-WO_3	100.0	56.0	S2
3	Porous $NbOPO_4$	68.0	39.3	S3
4	NbO/NbP	55.0	30.8	S4
5	1Nb-MMT-900	99.0	70.5	This work

Table S4 Summary of glucose conversion and 5-HMF yield under different condition [a]

Entry	Catalyst	Experimental parameter	
		Conversion/%	Yield/%
1	1Nb-MMT-900	99.0 ± 0.8	70.5 ± 2.0
2[b]	1Nb-MMT-900	98.7 ± 0.2	55.4 ± 1.9
3[c]	1Nb-MMT-900	98.7 ± 0.7	50.6 ± 0.7
4[d]	1Nb-MMT-900	91.5 ± 0.1	44.8 ± 2.6
5[e]	1Nb-MMT-900	95.0 ± 0.4	50.4 ±1.5
6[f]	1Nb-MMT-900	98.4 ± 0.7	65.6 ± 1.0

[a] Reaction conditions: 66.6 mM glucose, 40 mg catalyst, 170 °C, 3 h, 5 mL of reaction solution, methyl isobutyl ketone/saturated sodium chloride solution (MIBK-NaCl) =70 : 30 (v/v). [b, c] The initial concentration of glucose was 100 mM and 133 mM, respectively. [d, e, f] The initial mass of catalyst was 10 mg, 20 mg and 60 mg, respectively.

Table S5 Characterization of the recycled 1Nb-MMT-900 by XRF analysis.

Run	Si	Al	Ca	Mg	Fe	K	Na	P	Nb
Fresh	34.56	7.49	2.13	1.71	1.21	1.06	0.19	0.03	1.85
1	34.61	7.46	2.07	1.70	1.21	1.06	0.19	0.03	1.79
2	34.53	7.58	2.00	1.71	1.21	1.05	0.17	0.03	1.71
3	34.63	7.49	2.10	1.71	1.21	1.06	0.20	0.03	1.64
4	34.63	7.51	2.03	1.71	1.21	1.04	0.19	0.03	1.60

Table S6 5-HMF yield in two-phase solvent with different ratio of organic phase to inorganic phase (conditions: 66.6 mM glucose, 40 mg 1Nb-MMT-900, 170 ^{o}C, 3 h).

Entry	Volume of solvent (ml)		Yield/%		
	MIBK	Water (NaCl)	Organic phase	Inorganic phase	Total
1	5	0	7.44	0	7.44
2	4	1	44.92	8.1	53.02
3	3.5	1.5	51.17	19.35	70.52
4	3	2	31.84	15.89	47.73
5	2.5	2.5	25.44	17.16	42.6
6	1.5	3.5	14.12	23.13	37.25
7	0	5	0	15.56	15.56

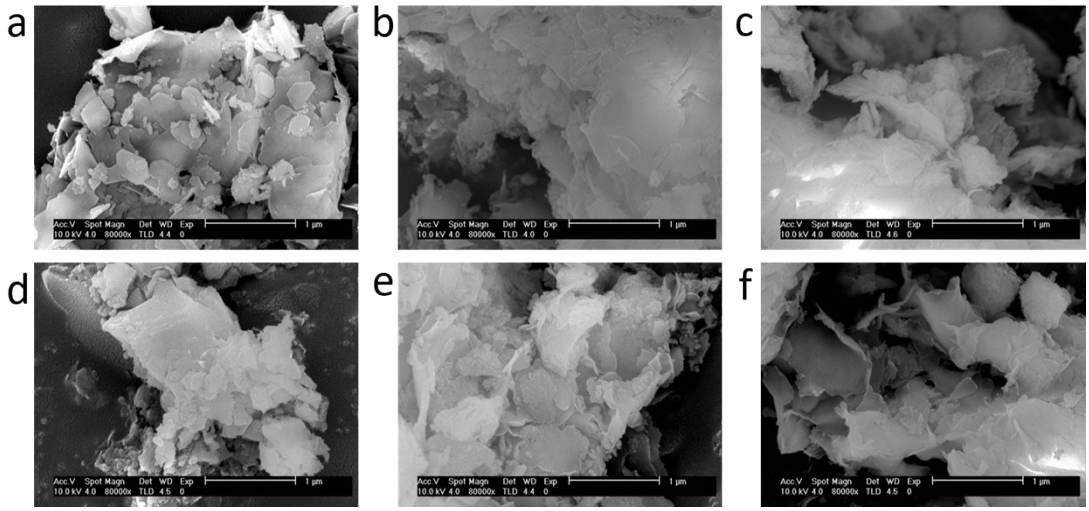

Fig. S1 SEM images of (a) MMT, (b) 0.25Nb-MMT, (c) 1Nb-MMT, (d) 3Nb-MMT, (e) 1Nb-MMT-500, and (f) 1Nb-MMT-900.

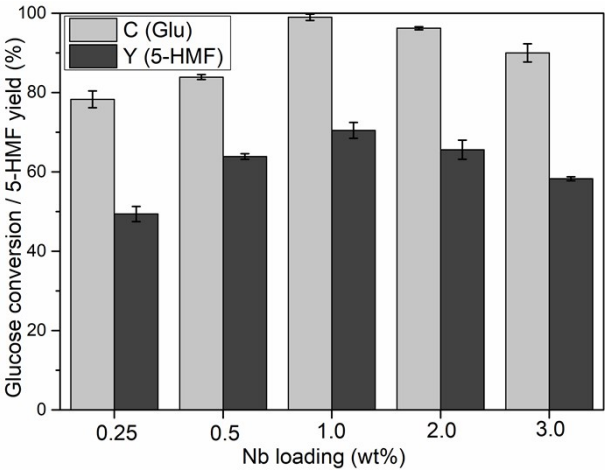

Fig. S2 The effect of different Nb loadings on glucose conversion and 5-HMF yield (conditions: 66.6 mM glucose, 40 mg 1Nb-MMT-900, 170 ^{o}C, 3 h, 5 mL of reaction solution, MIBK-NaCl =70 : 30 (v/v)).

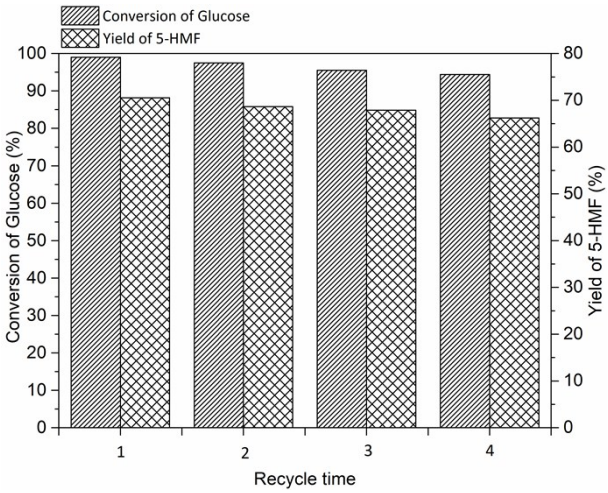

Fig. S3 Reusability of 1Nb-MMT-900 catalyst (conditions: 66.6 mM glucose, 40 mg 1Nb-MMT-900, 170 °C, 3 h, 5 mL of reaction solution, MIBK-NaCl =70 : 30 (v/v)).

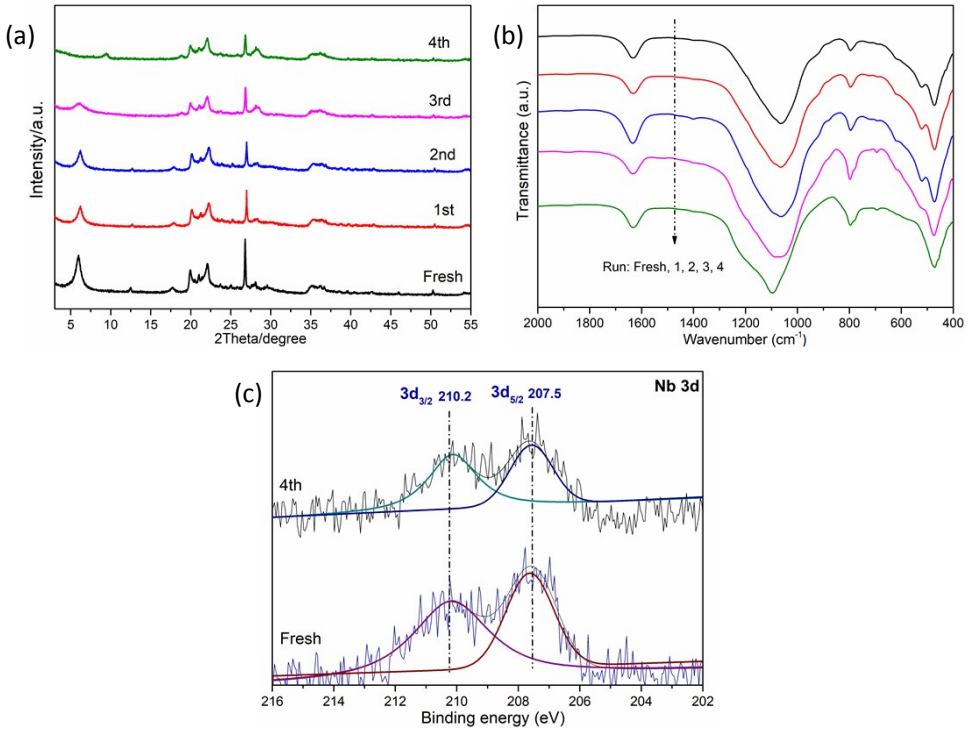

Fig. S4 XRD patterns (a), FTIR spectra (b), and XPS spectra (c) of 1Nb-MMT-900 during four consecutive runs.

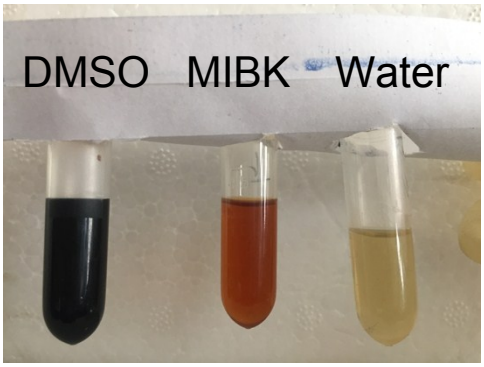

Fig. S5 Glucose conversion to 5-HMF in different solvents (conditions: 66.6 mM glucose, 40 mg 1Nb-MMT-900, 170 °C, 3 h).

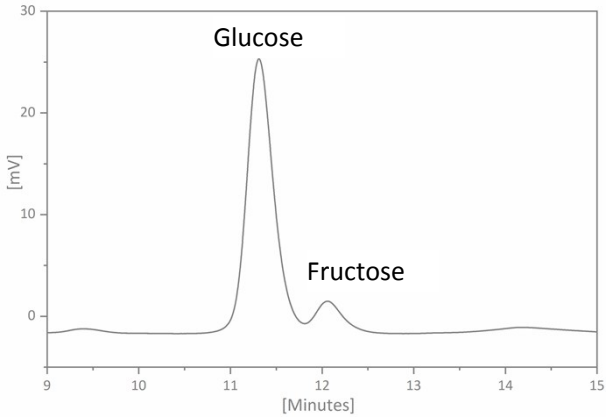

Fig. S6 HPLC chromatogram of the aqueous phase of the reaction solution obtained from the conversion of glucose (conditions: 66.6 mM glucose, 40 mg 1Nb-MMT-900, 170 °C, 5 min).

References

S1. K. Nakajima, Y. Baba, R. Noma, M. Kitano, J. N. Kondo, S. Hayashi and M. Hara, *J. Am. Chem. Soc.*, 2011, **133**, 4224-4227.

S2. C. Yue, G. Li, E. A. Pidko, J. J. Wiesfeld, M. Rigutto and E. J. Hensen, *Chemsuschem*, 2016, **9**, 2421-2429.

S3. Y. Zhang, J. Wang, X. Li, X. Liu, Y. Xia, B. Hu, G. Lu and Y. Wang, *Fuel*, 2015, **139**, 301-307.

S4. M. N. Catrinck, E. S. Ribeiro, R. S. Monteiro, R. M. Ribas, M. H. P. Barbosa and R. F. Teófilo, *Fuel*, 2017, **210**, 67-74.